

## REACTIONS WITH SUBSTITUTED XANTHONES—VI\*

### INFRARED SPECTRA OF HYDROXY-9-XANTHONES, HYDROXY-10-THIAXANTHONES AND SOME RELATED COMPOUNDS

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**Abstract**—Synthesis of 6'-substituted-4'-pyrono (2',3'-1,2)-(IIa and IIb), 4',5'-dihydro-4'-4-oxofurano (2',3'-1,2)-(IIIb and IIIc), 4',5'-dihydro-5'-methylfurano (2',3'-2,1)-(VI) and 4',5'-dihydro-5'-methylfurano (2',3'-4,3)-9-xanthones (VII) is described. The infrared absorption spectra of a number of hydroxy-9-xanthones, hydroxy-10-thioxanthones and new extended xanthone systems are briefly discussed.

In a previous publication,<sup>1</sup> it has been shown that 1-hydroxy-9-xanthone (IVa) is readily acylated under the conditions of the Fries and Friedel-Crafts reactions to give the corresponding 2-acyl-1-hydroxy-9-xanthone. Unlike 1-hydroxy-9-xanthone, the corresponding 2- and 4-hydroxy isomers<sup>1,2</sup> do not undergo the Friedel-Crafts reaction and the Fries rearrangement. In an attempt to find simple structural analogues of pharmacologically active chromones, such as khellin,<sup>3</sup> the synthesis of a number of new 2-acylated-1-hydroxy-9-xanthones (Ib–Ih) has been undertaken. Thus, 6'-methyl-4'-pyrono (2',3'-1,2)-9-xanthone (IIa) now has been obtained by cyclization of 2-( $\beta$ -chlorocrotonyl)-1-hydroxy-9-xanthone (Ig), obtained by the action of  $\beta$ -chlorocrotonyl chloride<sup>4</sup> on IVa in the presence of aluminium chloride. Attempts to prepare IIa via condensation of ethyl acetate with 2-acetyl-1-hydroxy-9-xanthone (Ia) or by the Kostanecki-Robinson reaction on Ia were reported by Suschitzky *et al.* to be unsuccessful.<sup>5</sup>



- |  |  |
|--|--|
| la, R = CH <sub>3</sub>                  | e, R = CH <sub>2</sub> · C <sub>6</sub> H <sub>5</sub> |
| b, R = CH <sub>2</sub> Cl                | f, R = CHBr · C <sub>6</sub> H <sub>5</sub>            |
| c, R = CH <sub>2</sub> · CH <sub>3</sub> | g, R = CH=C(Cl)CH <sub>3</sub>                         |
| d, R = CHBr · CH <sub>3</sub>            | h, R = CH=CH · C <sub>6</sub> H <sub>5</sub>           |

- IIa, R = CH<sub>3</sub>  
b, R = C<sub>6</sub>H<sub>5</sub>

Oxidation of 1-hydroxy-2-cinnamoyl-9-xanthone (Ih), obtained by the action of cinnamoyl chloride on 1-hydroxy-9-xanthone under the conditions of the Friedel-Crafts reaction, with selenium dioxide<sup>6</sup> effected the formation of 6'-phenyl-4'-pyrono

\* Part V., A. Mustafa, M. M. Sidky and F. M. Soliman, *Canad. J. Chem.* accepted for publication.

<sup>1</sup> A. Mustafa and O. H. Hishmat, *J. Amer. Chem. Soc.* **79**, 2225 (1957).

<sup>2</sup> F. Lamb and H. Suschitzky, *Tetrahedron* **5**, 1 (1959).

<sup>3</sup> C. P. Hutterer and E. Dale, *Chem. Rev.* **48**, 543 (1951); A. Schönberg and A. Sina, *J. Amer. Chem. Soc.* **72**, 1611 (1950).

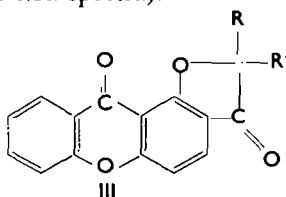
<sup>4</sup> cf. R. C. Elderfield *Heterocyclic Compounds* Vol. II p. 250. John Wiley (1951).

<sup>5</sup> J. S. H. Davies, F. Scheinmann and H. Suschitzky, *J. Chem. Soc.* 2140 (1956).

<sup>6</sup> H. S. Mahal, H. S. Rai and K. Venkataraman, *J. Chem. Soc.* 866 (1935).

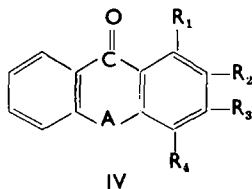
(2',3'-1,2)-9-xanthone (IIb). Compounds IIa and IIb respond positively to the known chromone and flavone tests. Thus, IIa gave a red-violet colour with potassium hydroxide pellets<sup>7</sup> and IIb produced an orange-red colouration on treatment with magnesium and hydrochloric acid.<sup>8</sup>

The furanoxanthone (IIIa) was obtained in a good yield by cyclization of the  $\omega$ -chloroderivative (Ib) with sodium acetate in ethanol. 2- $\omega$ -Chloroacetyl-1-hydroxy-9-xanthone (Ib) was prepared by the action of chloroacetyl chloride on IVa in the presence of aluminium chloride. Compound IIIa was found to be identical with 4',5'-dihydro-4'-oxofurano (2',3'-1,2)-9-xanthone described by Suschitzky *et al.*<sup>5</sup> (mixed m.p. and comparative I.R. spectra).



IIIa, R = R' = H  
 b, R = CH<sub>3</sub>, R' = H  
 c, R = C<sub>6</sub>H<sub>5</sub>, R' = H

Similarly, the 4',5'-dihydro-4'-oxofurano (2',3'-1,2)-9-xanthones IIIb and IIIc have been successfully obtained by cyclization of Id and If respectively. The bromo-ketones Id and If were prepared by the action of bromine in glacial acetic acid<sup>9</sup> on Ic and Ie respectively.



IVa, R <sub>1</sub> = OH, R <sub>2</sub> = R <sub>3</sub> = R <sub>4</sub> = H	A = O
b, R <sub>2</sub> = OH, R <sub>1</sub> = R <sub>3</sub> = R <sub>4</sub> = H	A = O
c, R <sub>4</sub> = OH, R <sub>1</sub> = R <sub>2</sub> = R <sub>3</sub> = H	A = O
d, R <sub>2</sub> = OH, R <sub>1</sub> = R <sub>3</sub> = R <sub>4</sub> = H	A = S
e, R <sub>1</sub> = CH <sub>3</sub> , R <sub>4</sub> = OH, R <sub>2</sub> = R <sub>3</sub> = H	A = S
f, R <sub>1</sub> = OH, R <sub>2</sub> = CH <sub>2</sub> .CH=CH <sub>2</sub> , R <sub>3</sub> = R <sub>4</sub> = H	A = O
g, R <sub>1</sub> = OH, R <sub>2</sub> = CH <sub>2</sub> .CHBr.CH <sub>3</sub> , R <sub>3</sub> = R <sub>4</sub> = H	A = O
h, R <sub>2</sub> = O.CH <sub>2</sub> .CH=CH <sub>2</sub> , R <sub>1</sub> = R <sub>3</sub> = R <sub>4</sub> = H	A = O
i, R <sub>2</sub> = OH, R <sub>1</sub> = CH <sub>2</sub> .CH=CH <sub>2</sub> , R <sub>3</sub> = R <sub>4</sub> = H	A = O
j, R <sub>2</sub> = OH, R <sub>1</sub> = CH <sub>2</sub> .CHBr.CH <sub>3</sub> , R <sub>3</sub> = R <sub>4</sub> = H	A = O
k, R <sub>4</sub> = O.CH <sub>2</sub> .CH=CH <sub>2</sub> , R <sub>1</sub> = R <sub>2</sub> = R <sub>3</sub> = H	A = O
l, R <sub>4</sub> = OH, R <sub>2</sub> = CH <sub>2</sub> .CH=CH <sub>2</sub> , R <sub>1</sub> = R <sub>3</sub> = H	A = O
m, R <sub>4</sub> = OH, R <sub>2</sub> = CH <sub>2</sub> .CHBr.CH <sub>3</sub> , R <sub>1</sub> = R <sub>3</sub> = H	A = O
n, R <sub>1</sub> = CH <sub>3</sub> , R <sub>4</sub> = O.CH <sub>2</sub> .CH=CH <sub>2</sub> , R <sub>2</sub> = R <sub>3</sub> = H	A = S
o, R <sub>1</sub> = CH <sub>3</sub> , R <sub>4</sub> = OH, R <sub>2</sub> = CH <sub>2</sub> .CH=CH <sub>2</sub> , R <sub>3</sub> = H	A = S

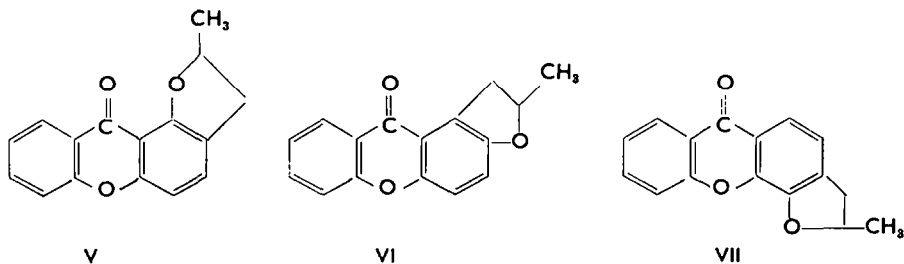
Recently, Scheinmann and Suschitzky<sup>10</sup> described the preparation of 4',5'-dihydro-5'-methylfuran (2',3'-1,2)-9-xanthone (V) via cyclization of 2- $\beta$ -bromopropyl-1-hydroxy-9-xanthone (IVg), obtained by saturating a solution of 2-allyl-1-hydroxy-9-xanthone (IVf) in glacial acetic acid with hydrogen bromide.

<sup>7</sup> A. Schönberg and A. Sina, *J. Chem. Soc.* 3344 (1950).

<sup>8</sup> T. A. Geissman and R. O. Clinton, *J. Amer. Chem. Soc.* **68**, 700 (1946).

<sup>9</sup> NG. PH. Buu-Hoi and D. Lavit, *J. Chem. Soc.* 18 (1955).

<sup>10</sup> F. Scheinmann and H. Suschitzky, *Tetrahedron* **7**, 31 (1959).



We now have investigated the preparation of the other isomeric furanoxanthenes, namely, 4',5'-dihydro-5'-methylfuranoxanthone (2',3'-2,1)-(VI) and 4',5'-dihydro-5'-methylfuranoxanthone (2',3'-4,3)-9-xanthone (VII). The 1-allyl-2-hydroxy- (IVi) and 3-allyl-4-hydroxy-9-xanthone (IVl) were obtained by a Claisen rearrangement of 2- (IVh) and 4-allyloxy-9-xanthone (IVk) effected by refluxing the ethers in dimethyl aniline respectively. Treatment of the obtained hydroxy-allyl-9-xanthenes (IVi and IVl) with hydrobromic acid (48%) in boiling acetic acid<sup>10</sup> gave 1- $\beta$ -bromopropyl-2-hydroxy-9-xanthone (IVj) and 3- $\beta$ -bromopropyl-4-hydroxy-9-xanthone (IVm) respectively. Cyclization of the bromo-compounds IVj and IVm by refluxing in ethanolic sodium ethoxide gave the corresponding furanoxanthenes VI and VII.

The 1-methyl-4-hydroxy-3-allyl-10-thioxanthone (IVO) was made similarly by a Claisen rearrangement of 1-methyl-4-allyloxy-10-thioxanthone (IVn).

The migration of the allyl group to the 1 position,<sup>11</sup> when IVh was subjected to Claisen rearrangement finds analogy with the behaviour of 2-hydroxy-9-xanthone (IVb) towards aminomethylation,<sup>12</sup> chloromethylation<sup>12</sup> and formylation<sup>13</sup> leading in all cases to substitution in the 1 position. The formation of 1-allyl-4-hydroxy-9-xanthone by the Claisen rearrangement of IVk should be excluded due to the fact that the bromo-compound IVm readily undergoes cyclization to the cyclized form VII. The structures of the furanoxanthenes VI and VII find support from their N.M.R. spectra\* which are in good agreement with the proposed structures, thus indicating the Markownikoff type of hydrogen bromide addition to the allyl-hydroxy-9-xanthenes IVi and IVl respectively.

#### *Carbonyl and hydroxyl absorption spectra in hydroxy-9-xanthone and hydroxy-10-thioxanthone derivatives*

1-Hydroxy-9-xanthone† (IVa) does not show a free OH absorption around  $3600\text{ cm}^{-1}$ . This may be attributed to the presence of intramolecular hydrogen

\* We wish to acknowledge our thanks to Professor Dr. H. Strehlow, Max-Planck Institut für Physikalische Chemie, Göttingen for carrying out the nuclear magnetic resonance and for helpful interpretations and discussions.

† By the time the present paper was being prepared for publication, the authors took notice of the abstract of a paper published by F. Scheinmann, *Chem. Abstr.* 57, 11979 (1962) dealing with the I.R. spectra of substituted and extended xanthenes.

As far as we can judge from the above mentioned summary, Scheinmann's results are in general conformity with ours.

<sup>11</sup> Reference should be made to relation of bond structure to Claisen rearrangement *Organic Reactions* Vol. II; p. 13. John Wiley, New York.

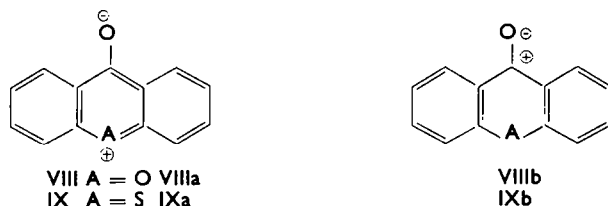
<sup>12</sup> A. Mustafa, M. M. Sidky and F. M. Soliman, *Canad. J. Chem.* accepted for publication.

<sup>13</sup> J. S. H. Davies, F. Lamb and H. Suschitzky, *J. Chem. Soc.* 1790 (1958).

bonding. Similar hydrogen bonded systems which lower the frequency of the OH-absorption are reported in the case of 5-hydroxyflavanone,<sup>14</sup> 5-hydroxy-flavone,<sup>14,15</sup> 1-hydroxyanthraquinone<sup>16</sup> and 1-hydroxyanthrone.<sup>16</sup>

Hydroxy-9-xanthenes having not internally bonded OH groups, e.g., 2-hydroxy-(IVb), and 4-hydroxy-9-xanthenes (IVc) show sharp OH-absorption which is at still lower frequency than normal (ca. 300  $\text{cm}^{-1}$  lower) (cf. Table 1). This may be due to intermolecular hydrogen bonding.<sup>17</sup> Another evidence for intermolecular hydrogen bonding in IVb and IVc may be illustrated in their melting points as compared with IVa. 4-Hydroxyanthrone and anthraquinones with non internally bonded OH-groups show similar behaviour.<sup>16</sup>

The carbonyl absorption of 1-, 2-, and 4-hydroxy-9-xanthenes (IVa-c) differ only slightly from each other and are close to that of unsubstituted 9-xanthone itself (Table 1). They all show a  $\nu(\text{C}=\text{O})$  around  $6.05 \mu$  due to the  $\gamma$ -pyrone carbonyl group.<sup>18</sup> The presence of an OH group in the *o*-position to the ring carbonyl causes only a slight shift in the  $\nu(\text{C}=\text{O})$  towards lower frequencies as compared with the xanthone carbonyl absorption ( $0.02 \mu$ ). The carbonyl absorption of 1-methoxy-9-xanthone ( $6.02 \mu$ ) is similar to that of 1-hydroxy-9-xanthone (IVa), which is in fact very close to that of 9-xanthone itself ( $6.0 \mu$ ). Thus, possibly structures VIIIa and VIIIb make very important resonance contributions to the structure of the 9-xanthone molecule.



The relative constancy of absorption in Nujol and in solution spectra of IVa affords additional support for the intramolecular nature of the hydrogen bond involving the hydroxyl and the xanthone carbonyl group. This indicates the difference of IVa from other hydroxy compounds, e.g. 1-hydroxyanthraquinone.<sup>16</sup> Analogous to IVa, 5-hydroxyflavone shows similar  $\nu(\text{C}=\text{O})$  as in flavone itself.<sup>14,15</sup> Thus, it may be concluded that there is no appreciable resonance interaction between the hydroxyl and the carbonyl groups in the studied hydroxy-9-xanthenes. Compounds IVb and IVc show a shift in the  $\nu(\text{C}=\text{O})$  of about  $0.07 \mu$  towards lower frequencies than VIII due to intermolecular hydrogen bonding. Etherification of the hydroxyl group with a methyl or allyl group restored nearly the characteristic  $\text{C}=\text{O}$  frequency (cf. Table 1).

The bands in the  $1625 \text{ cm}^{-1}$  (ca.  $6.15 \mu$ ) and  $1600 \text{ cm}^{-1}$  (ca.  $6.25 \mu$ ) region cannot be assigned unequivocally to the carbonyl group, since phenyl in plane-skeletal vibration can occur here. The intense band around  $6.15 \mu$  is commonly recorded in

<sup>14</sup> B. L. Shaw and T. H. Simpson, *J. Chem. Soc.* 655 (1955).

<sup>15</sup> J. H. Looker and W. W. Hanneman, *J. Org. Chem.* **27**, 381 (1962).

<sup>16</sup> M. St. Flett, *J. Chem. Soc.* 1441 (1948).

<sup>17</sup> Phenolic ketones are liable to certain intermolecular hydrogen bonding, cf. L. J. Ingraham, J. Corse, G. F. Baily and F. Stritt, *J. Amer. Chem. Soc.* **74**, 2297 (1952).

<sup>18</sup> The  $\epsilon$ -pyrone carbonyl absorption in 2-methylchromone (ref. 15) and in flavone absorb near this region, cf. E. G. Englett, *J. Org. Chem.* **23**, 93 (1958).

TABLE 1. HYDROXYL AND CARBONYL STRETCHING FREQUENCIES OF HYDROXY-9-XANTHONE AND HYDROXY-10-THIAXANTHONE DERIVATIVES

Compound	$\nu(\text{OH})$	$\nu(\text{C}=\text{O})$
	$\mu$	$\mu$
9-Xanthone (VIII)	—	6.0
1-Hydroxy-9-xanthone (IVa)	—	6.02; 6.02 <sup>a</sup>
1-Methoxy-9-xanthone	—	6.02
2-Hydroxy-9-xanthone (IVb)	3.0	6.07
2-Hydroxy-1-allyl-9-xanthone (IVi)	2.9	6.07
2-Methoxy-9-xanthone	—	6.02
2-Allyloxy-9-xanthone (IVh)	—	6.07
4-Hydroxy-9-xanthone (IVc)	3.0	6.07
4-Hydroxy-3-allyl-9-xanthone (IVj)	3.0	6.08
4-Hydroxy-3( $\beta$ -bromopropyl)-9-xanthone (IVm)	3.0	6.08
4-Methoxy-9-xanthone	—	6.02
4-Allyloxy-9-xanthone (IVk)	—	6.0
10-Thioxanthone (IX)	—	6.07
2-Hydroxy-10-thioxanthone (IVd)	2.9	6.13
2-Methoxy-10-thioxanthone	—	6.09
2-Allyloxy-10-thioxanthone	—	6.09
2-Acetoxy-10-thioxanthone	—	5.7 <sup>b</sup> and 6.07
1-Methyl-4-hydroxy-10-thioxanthone (IVe)	3.1	6.2
1-Methyl-3-allyl-4-hydroxy-10-thioxanthone (IVo)	3.05	6.18
1-Methyl-4-allyloxy-10-thioxanthone (IVn)	—	6.09
10-Thioxanthone sulphone	—	5.92
2-Hydroxy-10-thioxanthone sulphone	2.9	5.98

<sup>a</sup> In carbon tetrachloride.    <sup>b</sup> Ester (C=O).

conjugated unsaturated ketones and is associated with the stretching vibration of the C=C bonds,<sup>19</sup> and may be assigned for the 1,4-pyrone ring.<sup>15</sup>

10-Thioxanthone (IX) on the other hand, shows a small shift in the  $\nu(\text{C}=\text{O})$  towards lower frequencies than in VIII (0.07  $\mu$ ). This shift may be attributed to increased resonance arising from the lone pair of electrons on the sulphur atom. The 10-thioxanthone sulphone, on the other hand, shows normal  $\alpha,\beta$ -unsaturated carbonyl absorption (5.92  $\mu$ ). In sulphones, however, neither structure IXa or IXb are possible. This is in good agreement with the finding that, whereas, 1,4-thiapyrone does not absorb in the 1660  $\text{cm}^{-1}$  region (expected for a conjugated carbonyl group), thiapyrone sulphone shows a sharp absorption in the conjugated C=O and C=C double bond region.<sup>20</sup>

2-Hydroxy-10-thioxanthone (IVd) shows a sharp (OH) absorption (2.9  $\mu$ ). Similar to IVh, it shows a weak carbonyl absorption than in IX with a slight shift towards lower frequencies (0.07  $\mu$ ). Methylation or allylation restores the original carbonyl absorption. 2-Hydroxy-10-thioxanthone sulphone,<sup>20a</sup> on the other hand, shows the normal  $\alpha,\beta$ -unsaturated carbonyl absorption at 5.98  $\mu$ .

The 4-hydroxy-10-thioxanthenes IVe and IVo show very broad (OH) absorption appearing as a shoulder of the  $\nu(\text{C}-\text{H})$ . This is in contrast to 4-hydroxy-9-xanthone

<sup>19</sup> R. N. Jones, P. Humphries and K. Dobriner, *J. Amer. Chem. Soc.* **72**, 956 (1950).

<sup>20</sup> D. S. Tarbell and P. Hoffman, *J. Amer. Chem. Soc.* **76**, 2451 (1954).

<sup>20a</sup> W. B. Price and S. Smiles, *J. Chem. Soc.* 3159 (1928).

which shows sharper bands at relatively higher frequencies; thus indicating stronger hydrogen bonding in IVe and IVo. This shift in the  $\nu(\text{OH})$  in the latter compounds may be due to the possible internal chelation with the sulphur atom.

The 2-acyl-1-hydroxy-9-xanthenes (Ib–Ih), similar to 1-hydroxy-9-xanthone and to *o*-hydroxyaromatic ketones<sup>21</sup> show no free OH absorption owing to strong ring chelation. The OH-group may be involved in the intramolecular hydrogen bonding with either of the 2-acyl- or with the ring carbonyl group. The carbonyl absorption shows 2 bands between 5.9 and 6.15 due to the acyl carbonyl and xanthone C=O absorption respectively (cf. Table 2). The acyl carbonyl absorption lies near that of

TABLE 2.  $\epsilon(\text{C}=\text{O})$  AND  $\nu(\text{OH})$  OF 2-ACYL-1-HYDROXY-9-XANTHONES (Ib–Ih) AND OF THE EXTENDED XANTHONE SYSTEMS

Compound	$\nu(\text{OH})$	$\nu(\text{C}=\text{O})$	Xanthone
	$\mu$	$\mu$	$\begin{array}{c} \diagup \\ \text{C}=\text{O} \\ \diagdown \end{array}$ $\mu$
Ib	—	5.9	6.1
Ic	—	5.96	6.08
Id	—	5.94	6.08
Ie	—	5.98	6.08
If	—	5.9	6.08
Ig	—	6.0	6.15
Ih	—	6.0	6.12
IIa	—	5.94	6.08
IIb	—	6.0	6.07
IIIa	—	5.81	5.94
IIIb	—	5.81	5.94
V	—	—	6.0
VII	—	—	5.98

simple monoaryl ketones (ca.  $1685 \text{ cm}^{-1}$ ).<sup>21–23</sup> This may show the preference of the OH bonding with the ring carbonyl, as the  $\nu(\text{C}=\text{O})$  of the chelated *o*-hydroxyaromatic ketones is largely shifted towards lower frequencies (ca.  $1640 \text{ cm}^{-1}$ ).<sup>21</sup> The carbonyl absorption at  $6.0 \mu$  in Ig and Ih is due to the conjugated C=O in the 2 position and is comparable with that of benzal acetophenone ( $1667 \text{ cm}^{-1}$ ).<sup>24</sup>

The presence of an  $\alpha$ -bromine atom is known to effect the carbonyl maxima to a higher frequency (ca.  $20 \text{ cm}^{-1}$ ),<sup>25</sup> which is attributed to suppression of the carbonyl bond polarization by the halogen atom with increase in the double bond character of the carbonyl linkage.<sup>26</sup> This shift is smaller in Id than in Ib and If.

The pyronoxanthenes IIa and IIb show 2 carbonyl absorption maxima; that at higher frequency is attributed to the 2-methylchromone or flavone carbonyl.

<sup>21</sup> H. Hergert and E. F. Kurth, *J. Amer. Chem. Soc.* **75**, 1622 (1953); N. M. Cullinane, R. A. Wollhouse and V. V. B. Wood, *Rec. Trav. Chem.* **80**, 116 (1961).

<sup>22</sup> H. W. Tompson and P. Torkington, *J. Chem. Soc.* 640 (1945).

<sup>23</sup> N. Fuson, M. L. Josien and E. M. Shelton, *J. Amer. Chem. Soc.* **76**, 2526 (1954).

<sup>24</sup> I. M. Hunsberger, *J. Amer. Chem. Soc.* **72**, 5626 (1950).

<sup>25</sup> L. J. Bellamy *The Infra-Red Spectra of Complex Molecules* p. 139. John Wiley (1958).

<sup>26</sup> E. J. Hartwell, R. E. Richards and H. W. Thompson *J. Chem. Soc.*, 1436 (1948).

Similarly, III shows two carbonyl absorptions at 5.81 and 5.94  $\mu$ . The former is attributed to the frequency of the  $\text{>C=O}$  group of the coumaranone ring. This is favoured by the reported observation<sup>23</sup> that the carbonyl group in 5-membered ring systems absorbs at a higher frequency than in six membered ring systems (ca. 1750  $\text{cm}^{-1}$ ), a fact which is attributed to the increase in carbonyl character along with the increase in ring strain. Moreover, the presence of  $\alpha,\beta$ -unsaturated ketonic systems in the fused coumaranone ring with the xanthone ring would cause a shift towards lower frequency of ca. 38  $\text{cm}^{-1}$  (around 5.8  $\mu$ ). The xanthone carbonyl absorption in III, V and VII is slightly shifted towards higher frequencies, presumably due to increased resonance in these structures.

### EXPERIMENTAL

All m.p.s are uncorrected. The I.R. absorption spectra were determined in Nujol with a Perkin-Elmer Infracord Spectrophotometer Model 137.

**2-Acylated-9-xanthenes.** A mixture of 1-hydroxy-9-xanthone<sup>27</sup> (0.01 mole) and powdered anhydrous aluminium chloride (0.025 mole) in nitrobenzene (25 ml) was treated portionwise under stirring with a solution of the acyl chloride (0.012 mole) in nitrobenzene (5 ml). The reaction mixture was heated for 3 hr (steam-bath) and kept at room temp overnight. After decomposition with 2 N HCl, the mixture was subjected to steam distillation to remove nitrobenzene. The solid residue, so obtained, was then extracted with hot pet ether (b.p. 100–120°). Concentration and cooling of the extract gave the corresponding 2-acyl-derivative which was crystallized from the proper solvent. Yields, physical and analytical data of these compounds are given in Table 3.

**6'-Methyl-4'-pyrro- (2',3'-1,2)-9-xanthone (IIa).** A solution of 2-( $\beta$ -chlorocrotonoyl)-1-hydroxy-9-xanthone (1.57 g) in absolute ethanol (400 ml) was refluxed for 2 hr in presence of crystalline sodium acetate (3 g). After removing of the alcohol under reduced pressure, 10% dilute hydrochloric acid (50 ml) was added. The precipitate obtained was collected, washed with water and crystallized from ethanol to give IIa as colourless crystals, m.p. 244–246° (1.2 g 85%) (Found: C, 73.49; H, 3.36.  $\text{C}_{17}\text{H}_{10}\text{O}_4$  requires: C, 73.37; H, 3.62%). IIa gave a red-violet colour when admixed with moistened potassium hydroxide pellets.

**6'-Phenyl-4'-pyrro- (2',3'-1,2)-9-xanthone (IIb).** 2-Cinnamoyl-1-hydroxy-9-xanthone (3.4 g) was refluxed in isoamyl alcohol (50 ml) with selenium dioxide (3.5 g) for 12 hr. After cooling, the resulting precipitate was collected and crystallized from isoamyl alcohol to give IIb as colourless crystals, m.p. 296–298° (2.7 g 80%) (Found: C, 77.37; H, 3.34.  $\text{C}_{21}\text{H}_{14}\text{O}_4$  requires: C, 77.64; H, 3.55%). Compound IIb gave no ferric chloride reaction and on treatment, in alcoholic solution, with magnesium and hydrochloric acid gave an orange-red colour at room temp.

**4',5'-Dihydro-4'-oxofurano (2',3'-1,2)-9-xanthone (IIIa).** The furanoxanthenone (IIIa) was obtained by refluxing 2-*o*-chloroacetyl-1-hydroxy-9-xanthone (0.28 g) with crystalline sodium acetate (0.4 g) in ethanol (150 ml) for 1 hr. Recrystallization from ethanol gave IIIa as colourless crystals, m.p. 252–254° (0.21 g, 84%). IIIa proved to be identical with authentic 4',5'-dihydro-4'-oxofurano (2',3'-1,2)-9-xanthone<sup>4</sup> by mixed m.p. and comparative I.R. spectra.

**4',5'-Dihydro-5'-methyl-4'-oxofurano(2',3'-1,2)-9-xanthone (IIIb).** 2-Propionyl-1-hydroxy-9-xanthone (1.34 g) in glacial acetic acid (100 ml) was treated dropwise with bromine (0.8 g) in glacial acetic acid (10 ml) and the mixture was heated at 80° for 1 hr. The yellow crystals which separated on cooling were collected and recrystallized from glacial acetic acid to give 2-( $\alpha$ -bromopropionyl)-1-hydroxy-9-xanthone (Id) as yellow crystals, m.p. 132° (des) (1.4 g, 82%) (Found: Br, 23.21.  $\text{C}_{16}\text{H}_{11}\text{O}_4$  Br requires: Br, 23.01%). A solution of the bromoketone (Id, 1.73 g) in ethanol (200 ml) was refluxed for 2 hr in presence of crystalline sodium acetate (2 g). After removing the alcohol in a vacuum, the solid residue obtained was treated with 10% dilute hydrochloric acid, filtered, washed with water and crystallized from ethanol to give IIIb as colourless crystals, m.p., 238° (0.79 g, 60%) (Found: C, 72.06; H, 3.97.  $\text{C}_{16}\text{H}_{10}\text{O}_4$  requires: C, 72.17; H, 3.78%). IIIb gave a negative ferric chloride colour reaction.

**4',5'-Dihydro-5'-phenyl-4'-oxofurano(2',3'-1,2)-9-xanthone (IIIc).** The bromo-ketone (If) was

<sup>27</sup> K. S. Pankajamani and T. R. Seshadri, *J. Sci. Ind. Res. India* **13B**, 396 (1954).

TABLE 3. SUBSTITUTED HYDROXY-9-XANTHONES AND HYDROXY-10-THIAOXANTHONES

Xanthone derivative	Yield %	M.P.	Found(%)			Cl or S	Formula	Required(%)		
			C	H	Cl or S			C	H	Cl or S
Ib	86%	228 <sup>oa</sup>	—	—	Cl, 12:35	C <sub>15</sub> H <sub>9</sub> O <sub>4</sub> Cl	—	—	Cl, 12:28	
Ic	70%	184 <sup>oa</sup>	71.72	4.58	—	C <sub>16</sub> H <sub>13</sub> O <sub>4</sub>	71.63	4.50	—	
Ie	63%	156 <sup>oa</sup>	76.62	4.43	—	C <sub>17</sub> H <sub>11</sub> O <sub>4</sub>	76.82	3.68	—	
Ig	80%	156 <sup>oa</sup>	—	—	Cl, 11:26	C <sub>17</sub> H <sub>11</sub> O <sub>4</sub> Cl	—	—	Cl, 11:26	
Ih	90%	196 <sup>ob</sup>	77.52	4.44	—	C <sub>16</sub> H <sub>11</sub> O <sub>4</sub>	77.18	4.12	—	
IVh	79%	106 <sup>oc</sup>	75.78	4.99	—	C <sub>16</sub> H <sub>15</sub> O <sub>3</sub>	76.17	4.79	—	
IVi	85%	211 <sup>od</sup>	76.36	5.19	—	C <sub>16</sub> H <sub>15</sub> O <sub>3</sub>	76.17	4.79	—	
IVk	80%	149 <sup>oc</sup>	76.37	5.11	—	C <sub>16</sub> H <sub>15</sub> O <sub>3</sub>	76.17	4.79	—	
IVl	85%	222 <sup>od</sup>	76.25	5.16	—	C <sub>16</sub> H <sub>15</sub> O <sub>3</sub>	76.17	4.79	—	
IVn	78%	110 <sup>oc</sup>	72.30	5.06	S, 11:37	C <sub>17</sub> H <sub>14</sub> O <sub>2</sub> S	72.31	4.99	S, 11:35	
IVo	85%	223 <sup>od</sup>	72.38	5.27	S, 11:99	C <sub>17</sub> H <sub>14</sub> O <sub>2</sub> S	72.31	4.99	S, 11:35	

<sup>a</sup> Crystallizing solvent was glacial acetic acid <sup>b</sup> Crystallized from isoamyl alcohol.<sup>c</sup> Pet ether (b.p. 70-80°) was used as a solvent for crystallization. <sup>d</sup> Crystallized from solvent ethanol.



prepared from 2-phenylacetyl-1-hydroxy-9-xanthone (Ie) using the same procedure described for the preparation of 2-( $\alpha$ -bromopropionyl)-1-hydroxy-9-xanthone (Id). It was crystallized from glacial acetic acid as yellow crystals, m.p. 155° (dec) (55°) (Found: Br, 20.12.  $C_{21}H_{13}O_4Br$  requires: Br, 19.52%). The oxofurano-9-xanthone derivative IIIc was obtained by cyclization of the bromo-ketone (If) in a manner similar to that of Id to form IIIb. Recrystallization from dioxan gave IIIc as colourless crystals, m.p. 315–317° (20%) (Found: C, 76.43; H, 3.71.  $C_{21}H_{12}O_4$  requires: C, 76.82; H, 3.68%).

*Allyloxy-9-xanthenes* (IVh and IVk) and *allyloxy-10-thioxanthone* (IVn). The allyloxy derivatives IVh, IVk and IVn were prepared by heating the corresponding hydroxanthenes<sup>28</sup> (0.01 mole) with excess allyl bromide (0.02 mole) and potassium carbonate (10 g) in dry acetone (75 ml) for 24 hr. After separating the inorganic residue, the excess of allyl bromide and acetone was removed under red. press. The solid products were crystallized from the appropriate solvents (cf. Table 3).

*Claisen rearrangement of allyloxy-9-xanthenes* (IVh and IVk) and *allyloxy-10-thioxanthone* (IVn). The allyloxyxanthone derivative (Ig) in dimethylaniline (10 ml) was heated under reflux for 3 hr. Acidification with aqueous hydrochloric acid (2N) precipitated the corresponding allyl-hydroxy-xanthone derivative in almost theoretical yield (cf. Table 3).

*4',5'-Dihydro-5'-methylfurano (2':3'-2:1)-9-xanthone* (VI). A mixture of 1-allyl-2-hydroxy-9-xanthone (0.75 g), bromine-free aqueous hydrobromic acid (48% 15 ml) and glacial acetic acid (5 ml) was boiled under reflux for 45 min. The solid material obtained by pouring the reaction mixture into ice-water was crystallized from ethanol to give IVj as red-brown crystals, m.p. 252–253° (0.6 g, 61%) (Found: Br, 23.77.  $C_{16}H_{13}O_3Br$  requires: Br, 23.98%). 1- $\beta$ -Bromopropyl-2-hydroxy-9-xanthone (IVj; 0.6 g) was boiled in ethanolic sodium ethoxide (0.1 g sodium in 50 ml ethanol) for 2 hr. The major part of the solvent was removed under red. press. Addition of 10% dilute hydrochloric acid precipitated a solid which was crystallized from pet ether (b.p. 110–140°) to give 4',5'-dihydro-5'-methylfurano (2',3'-2,1)-9-xanthone as pale yellow crystals, m.p. 158–160° (0.2 g, 44%) (Found: C, 76.45; H, 5.07.  $C_{16}H_{12}O_3$  requires: C, 76.17; H, 4.79%).

*4',5'-Dihydro-5'-methylfurano(2',3'-4,3)-9-xanthone* (VII). 3- $\beta$ -Bromopropyl-4-hydroxy-9-xanthone (IVm) was obtained from 3-allyl-4-hydroxy-9-xanthone (IVk) following the same procedure described for the preparation of IVj. Crystallization from ethanol gave the analytical sample, m.p. 225–226° (Found: Br, 23.77.  $C_{16}H_{13}O_3Br$  requires: Br, 23.98%). It was cyclized by refluxing in ethanolic sodium ethoxide to give 4',5'-dihydro-5'-methylfurano (2',3'-4,3)-9-xanthone, m.p. 139° from pet ether (80–110°) (Found: C, 76.72; H, 5.06.  $C_{16}H_{12}O_3$  requires: C, 76.17; H, 4.79%).

<sup>28</sup> For the preparation of 2- and 4-hydroxy-9-xanthone, see F. Ullmann and M. Zlokasoff, *Ber. Dtsch. Chem. Ges.* **38**, 2111 (1905); R. N. Sen and S. C. Sen-Gupta, *J. Indian Chem. Soc.* **6**, 267 (1929) for 1-methyl-4-hydroxy-10-thioxanthone.