

List of Published Papers.

1. A New One Step Synthesis of Xanthenes by R.J. Patolia and K.N. Trivedi, Chem. Ind. 235 (1978).
2. Studies in the Synthesis of Xanthone Derivatives Part I : Synthesis of Furoxanthenes by K.P. Shanghvi, R.J. Patolia and K.N. Trivedi, J. Indian Chem. Soc., 56, 52-5 (1979).
3. Studies in the Synthesis of Furochromones Part VII by R.J. Patolia and K.N. Trivedi, J. Indian Chem. Soc., (In Press).
4. Studies in the Synthesis of Xanthone Derivatives Part II : Synthesis of Furoxanthenes by R.J. Patolia, K.P. Shanghvi and K.N. Trivedi, J. Indian Chem. Soc., (In Press).

# new one step synthesis of xanthenes

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xanthenes and their derivatives have been prepared by condensation of *o*-hydroxybenzoic acid derivatives with monohydric, dihydric and trihydric phenols in the presence of a condensing agent such as acetic anhydride, Lewis acid catalysts, a mixture of phosphorus oxychloride and zinc chloride or PPA. In continuation of work<sup>1</sup> on the synthesis of benzo- $\gamma$ -pyrone, a new synthesis of xanthone derivatives is now reported. Smooth condensation of the ethyl or a methyl ester of an *o*-hydroxy-aromatic acid and a phenol is achieved by heating the mixture under reflux in biphenyl ether, without addition of a condensing agent.

Phenols, such as phloroglucinol, orcinol, pyrogallol,  $\alpha$ -naphthol or  $\beta$ -naphthol, when condensed with ethyl salicylate, give directly the corresponding xanthone derivatives. Whereas phenols like resorcinol, 2-methylresorcinol and catechol, give the corresponding hydroxyxanthenes as well as the intermediate benzophenone derivatives, less reactive phenols such as resorcinol and 3,4-*o*-xylenol give only the corresponding benzophenone derivatives, which are dehydrated to the corresponding methyl or dimethyl xanthenes by concentrated sulphuric acid (85 per cent). In the case of resorcinol, a mixture of 1-hydroxy- and 3-hydroxyxanthone was obtained in which 3-hydroxyxanthone was preponderant. With orcinol, 1-hydroxy-3-methyl- and 3-hydroxy-1-methylxanthone were obtained, the former as the major product.

These results indicate that  $\gamma$ -substitution in the resorcinol

nucleus took place in both cases, which is rather difficult without a condensing agent. A similar observation was made during the condensation of resorcinol with diethyl benzylmalonate.<sup>2</sup>

A mixture of an ethyl ester of an *o*-hydroxybenzoic acid and a phenol (1:1mol) is dissolved in the minimum quantity of hot biphenyl ether and is heated under reflux for 1 to 25h, depending upon the reactivity of the phenol. The cooled reaction mixture is diluted with light petroleum or steam distilled and the separated crude product was washed successively with cold sodium hydrogen carbonate to remove any hydrolysed acid and water. The product, a hydroxybenzophenone or a xanthone derivative is suitably purified by passage through a column of alumina (if necessary), followed by crystallisation from an appropriate solvent. Yields vary from 30–65 per cent. All the compounds gave satisfactory elemental analyses and were characterised by the preparation of their methyl ether or acetyl derivatives and by measurements of their infrared and n.m.r. spectra.

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- <sup>2</sup> Trivedi, K. N., *Curr. Sci.*, 1961, 30, 54

# Studies in the Synthesis of Xanthone Derivatives. Part-I

## Synthesis of Furanoxanthenes

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2-Methylresorcinol, on thermal condensation with ethyl cyclohexanone-2-carboxylate in diphenyl ether gave 6-hydroxy-5-methyl-1,2,3,4-tetrahydroxanthone, which on allylation, Claisen migration, cyclisation with conc. sulphuric acid followed by dehydrogenation with palladised charcoal, gave 4, 5'-dimethylfurano(3', 2'-2,3)xanthone (III). (III), was also synthesised from 3-hydroxy-4-methylxanthone by similar series of reactions. 5'-Methylfurano(2',3'-3,4)xanthone (V) was synthesised, starting from resorcinol and ethyl cyclohexanone-2-carboxylate and also from 3-hydroxyxanthone. The structures of intermediate dihydrofuranoxanthenes were confirmed by NMR spectra.

THE synthesis of linear or angular type of Furanoxanthenes have been reported by many workers<sup>1-6</sup>. The synthesis of angular furano compounds is simple, while a linear isomer needs a blocking group<sup>6</sup> like an acetyl or a methyl group in order that the Claisen migration of an allyloxy derivative produces an appropriate intermediate for the synthesis of a linear furano compound. Rajagopal and co-workers<sup>4</sup> have used this procedure for the synthesis of linear furanoxanthenes.

In general, two approaches have been used for the building up of a furan ring especially for  $\alpha$ -methyl furano derivatives. The one based on Scheinmann and Suschitzky's work<sup>1</sup>, gives dihydrofurano compounds, which were dehydrogenated by treatment with N-bromosuccinimide in presence of benzoyl peroxide followed by dehydrobromination with pyridine. The second route is an adaptation of the method of Admas and Rindfusz<sup>7</sup> involving addition of bromine to *o*-acetoxy-allyl derivatives followed by cyclisation and dehydrobromination by alcoholic alkali. Rajagopal and co-workers adopted second route for the synthesis of 4, 5'-dimethylfurano (3',2'-2,3)xanthone(III)<sup>8</sup>, while 5'-methylfurano (2',3'-3,4)xanthone(V)<sup>9</sup> was synthesised by both the methods,

In the present work, *o*-hydroxy-allylxanthenes were converted into dihydrofuranoxanthenes using conc. sulphuric acid, according to Shaikh and Trivedi<sup>10</sup>. This method is very convenient and gives quantitative yields of dihydrofuranoxanthenes, which on dehydrogenation with DDQ in benzene or with palladised charcoal in diphenyl ether gave the corresponding  $\alpha$ -methylfuranoxanthenes.

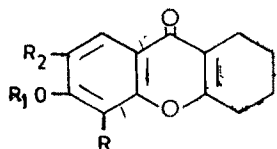
Condensation of 2-methylresorcinol with ethyl cyclohexanone-2-carboxylate in boiling diphenyl ether, according to Desai, Trivedi and Sethna<sup>11</sup>

gave 6-hydroxy-5-methyl-1,2,3,4-tetrahydroxanthone (Ia). This on allylation followed by Claisen migration gave 7-allyl-6-hydroxy-5-methyl-1, 2, 3, 4-tetrahydroxanthone (Ic). Cyclisation of (Ic) by trituration with conc. sulphuric acid afforded 5,5'-dimethyl-1,2,3,4,4',5'-hexahydrofurano (2',3'-6,7) xanthone(II).

Dehydrogenation of (II) by palladised charcoal (10%) furnished 4, 5'-dimethylfurano (3', 2'-2, 3) xanthone (III). (III), was also synthesised by carrying out allylation of 3-hydroxy-4-methylxanthone<sup>8</sup> which on Claisen migration gave (VIb). (VIb), was cyclised with conc. sulphuric acid to yield dihydrofurano-xanthone (VII). The structure of (VII) was confirmed by NMR spectrum (CDCl<sub>3</sub>):  $\delta$ 1.65, 3H doublet,  $J=7$ Hz, CH<sub>3</sub> group at C5'-CH<sub>3</sub>; 2.47, 3H singlet, -CH<sub>3</sub> group at C4-CH<sub>3</sub>; 2.9-3.7, 2H multiplet<sup>a</sup> at C4'-H<sub>2</sub>; 5.15, 1H quartet,  $J=7$ Hz, at C5'-H; 7.3-7.8, 3H multiplet, at C5-H, C6-H and C7-H (aromatic); 8.0, 1H singlet, at C<sub>1</sub>-H; 8.35, 1H<sup>a</sup> doublet,  $J=9$ Hz, at C8-H. This on dehydrogenation with DDQ in dry benzene gave (III). The mixed m. p. of the compounds prepared by the above procedures remained undepressed.

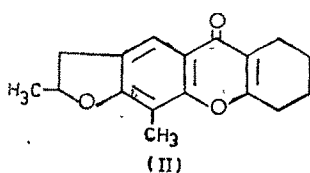
Similarly, resorcinol was condensed with ethyl cyclohexanone-2-carboxylate in diphenyl ether to give 6-hydroxy-1,2,3, 4-tetrahydroxanthone (Id)<sup>12</sup>. (Id), on allylation followed by Claisen migration gave 5-allyl-6hydroxy-1, 2, 3, 4-tetrahydroxanthone (If), which on cyclisation with conc. sulphuric acid afforded 5'-methyl-1, 2, 3, 4, 4', 5'-hexahydrofurano (3',2'-5,6) xanthone (IV), which was dehydrogenated with palladised charcoal to 5'-methylfurano-(2',3'-3,4) xanthone (V). (V), was also synthesised from 3-hydroxyxanthone by carrying out allylation, Claisen migration and cyclisation with conc. sulphuric acid, followed by dehydrogenation with palladised charcoal. The structure of (V) was confirmed by NMR spectrum (CDCl<sub>3</sub>):  $\delta$ 2.6, 3H singlet, -CH<sub>3</sub><sup>a</sup>

group at C5'-CH<sub>3</sub>; 6.84, 1H singlet, at C4'-H; 7.45-7.8, 4H multiplet, at C<sub>8</sub>-H, C5-H, C6-H and C7-H (aromatic); 8.32, 1H doublet, J=9Hz, at C1-H; 8.5, 1H doublet, J=9Hz, at C8-H. The mixed m. p. of the compounds (V), obtained by both the procedures, remained undepressed.

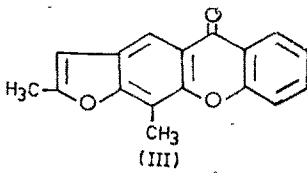


(I)

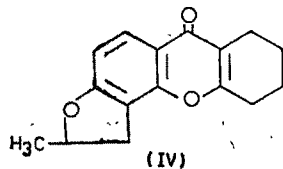
- |  |   |
|--|---|
| (Ia) R=CH <sub>3</sub> .                     | R <sub>1</sub> =R <sub>2</sub> =H                                       |
| (Ib) R=CH <sub>3</sub> .                     | R <sub>1</sub> =-CH <sub>2</sub> CH=CH <sub>2</sub> , R <sub>2</sub> =H |
| (Ic) R=CH <sub>3</sub> .                     | R <sub>1</sub> =H, R <sub>2</sub> =-CH <sub>2</sub> CH=CH <sub>2</sub>  |
| (Id) R=R <sub>1</sub> =R <sub>2</sub> =H     |   |
| (Ie) R=R <sub>2</sub> =H,                    | R <sub>1</sub> =-CH <sub>2</sub> CH=CH <sub>2</sub>                     |
| (If) R=-CH <sub>2</sub> CH=CH <sub>2</sub> , | R <sub>1</sub> =R <sub>2</sub> =H                                       |



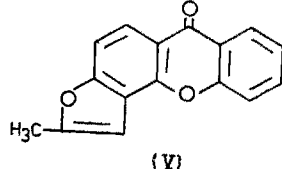
(II)



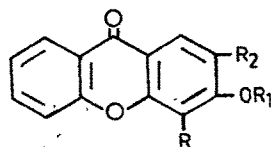
(III)



(IV)

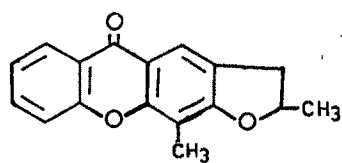


(V)

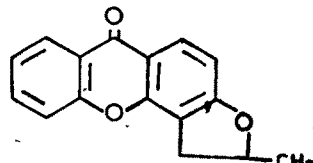


(VI)

- |  |   |
|--|---|
| (VIa) R=CH <sub>3</sub> .                      | R <sub>1</sub> =-CH <sub>2</sub> CH=CH <sub>2</sub> , R <sub>2</sub> =H |
| (VIb) R=CH <sub>3</sub> .                      | R <sub>1</sub> =H, R <sub>2</sub> =-CH <sub>2</sub> CH=CH <sub>2</sub>  |
| (VIc) R=R <sub>2</sub> =H,                     | R <sub>1</sub> =-CH <sub>2</sub> CH=CH <sub>2</sub>                     |
| (VI d) R=-CH <sub>2</sub> CH=CH <sub>2</sub> , | R <sub>1</sub> =R <sub>2</sub> =H                                       |



(VII)



(VIII)

## Experimental

### 6-Hydroxy-5-methyl-1, 2, 3, tetrahydroxanthone (Ia) :

A mixture of 2-methylresorcinol (3 g) and ethyl cyclohexanone-2-carboxylate (4 ml) was refluxed with diphenyl ether (10 ml) for 3 hr., with a short

condenser to facilitate the removal of alcohol formed. After cooling, the separated product was filtered and washed several times with petroleum ether. It crystallised from dimethyl formamide, m.p. 270°. Yield 2g (Found : C, 72.90; H, 6.08. C<sub>14</sub>H<sub>14</sub>O<sub>3</sub> requires C, 73.05; H, 6.08%)

### 6-Allyloxy-5-methyl-1,2,3,4-tetrahydroxanthone (Ib) :

A mixture of 6-hydroxy-5-methyl-1,2,3,4-tetrahydroxanthone (2g), allylbromide (1g) and anhydrous potassium carbonate (8 g) was refluxed in dry acetone (200 ml) in water bath for 10 hr. The reaction mixture was poured into water. The separated product was filtered, washed with very dilute sodium hydroxide solution to remove unreacted compound, the product crystallised from benzene-petroleum ether, m.p. 110°. Yield 1.5g (Found : C, 75.68; H, 6.34. C<sub>17</sub>H<sub>18</sub>O<sub>3</sub> requires C, 75.53; H, 6.66%)

### 7-Allyl-6-hydroxy-5-methyl-1,2,3,4-tetrahydroxanthone (Ic) :

6-Allyloxy-5-methyl-1, 2, 3, 4-tetrahydroxanthone (2g) was refluxed with dimethylaniline (10 ml) for 8 hr. After cooling, the reaction mixture was poured into conc. hydrochloric acid (50 ml) containing pieces of ice, the separated product was filtered and dissolved in sodium hydroxide solution. The solution was filtered. The filtrate on acidification with conc. hydrochloric acid gave the product, which was crystallised from alcohol. M.p. 221°, yield 1.5 g (Found : C, 75.26; H, 6.20. C<sub>17</sub>H<sub>18</sub>O<sub>3</sub> requires C, 75.53; H, 6.66%). IR spectrum : 1625 cm<sup>-1</sup> (ν-pyronyl>C=O group) and a broad band at 3500 cm<sup>-1</sup> (aromatic-OH group).

### 5,5',-Dimethyl-1,2,3,4,4',5'-hexahydrofurano(2',3'-6,7) xanthone(II)

7-Allyl-6-hydroxy-5-methyl-1,2,3,4-tetrahydroxanthone (1g) was triturated with conc. sulphuric acid (5 ml) in a water bath for 15 minutes. The contents were poured into crushed ice, the separated product

was filtered and washed with dilute sodium hydroxide solution to remove uncyclised compound. It crystallised from alcohol, m. p. 210°, yield 0.8. (Found : C, 75.18; H, 6.35. C<sub>17</sub>H<sub>18</sub>O<sub>3</sub> requires C, 75.53; H, 6.66%). IR spectrum 1635 cm<sup>-1</sup> (ν-pyronyl>C=O group).

$\lambda_{\text{max}}^{\text{chloroform}}$  248 nm (log e 4.22), 255 nm (log e 4.24), 304 nm (log e 4.18).

**4,5'-Dimethylfurano (3',2'-2,3)xanthone (III) :**

A mixture of 5,5'-dimethyl-1,2,3,4,4',5'-hexahydrofurano (2',3'-6,7)xanthone (0.5 g) palladised charcoal (10%, 0.3 g) and diphenyl ether (5 ml) was refluxed for 10 hr. The reaction mixture was filtered hot and after cooling, petroleum ether was added to the filtrate. The separated product was filtered and washed several times with petroleum ether. It crystallised from acetic acid, m.p. 242°. Yield 0.25 g. (Found : C, 77.00; H, 4.34.  $C_{17}H_{12}O_3$  requires C, 77.27; H, 4.55%).

IR spectrum  $1640\text{ cm}^{-1}$  ( $\gamma$ -pyronyl  $>C=O$  group);  $880\text{ cm}^{-1}$  (furan ring).

$\lambda_{\text{max}}^{\text{Methanol}}$  255 nm (log e 3.90), 290 nm (log e 3.10), 300 nm (log e 3.12), 360 nm (log e 2.84).

**3-Allyloxy-4-methylxanthone (VIa) :**

A mixture of 3-hydroxy-4-methylxanthone (2.5 g), allylbromide (2 g) and anhydrous potassium carbonate (12 g) was refluxed in dry acetone (300 ml) in a water bath for 11 hr. The reaction mixture was worked up as described above. The product crystallised from benzene-petroleum ether, m.p. 149° (lit<sup>8</sup>, m.p. 144°). Yield 3 g. (Found : C, 76.19; H, 5.02.  $C_{17}H_{14}O_3$  requires C, 76.67; H, 5.26%).

**2-Allyl-3-hydroxy-4-methylxanthone (VIb) :**

3-Allyloxy-4-methylxanthone (2.5 g) in dimethylaniline was refluxed for 4 hr. The reaction mixture was worked up as described above. The product crystallised from alcohol, m.p. 168°. Yield 2.2 g (lit<sup>8</sup>, m.p. 165°) (Found : C, 76.47; H, 5.56.  $C_{17}H_{14}O_3$  requires C, 76.67; H, 5.26%). IR spectrum  $1635\text{ cm}^{-1}$  ( $\gamma$ -pyronyl  $>C=O$  group) and a broad band at  $3200\text{ cm}^{-1}$  (aromatic -OH group).

**4,5'-Dimethyl-4'-5'-dihydrofurano(3',2'-2,3)xanthone (VII) :**

2-Allyl-3-hydroxy-4-methylxanthone (1.5 g) was triturated with sulphuric acid (85%, 9 ml) in a water bath for 15 minutes. The reaction mixture was worked up as described above. It crystallised from alcohol and then from benzene-petroleum ether. M.p. 174°. Yield 1 g. (Found : C, 77.13; H, 5.14.  $C_{17}H_{14}O_3$ ; requires C, 76.67; H, 5.26%).

**4,5'-Dimethylfurano (3'2'-2,3)xanthone (III) :**

A mixture of 4,5'-dimethyl-4',5'-dihydrofurano (3',2'-2,3) xanthone (0.6 g) and DDQ (0.535 g) was refluxed in sodium dried benzene (30 ml) in a water bath for 6 hr. The separated product was filtered off and the filtrate on evaporation gave solid, which crystallised from acetic acid and also from benzene-petroleum ether, m.p. 242° (lit<sup>8</sup>, m.p. 235°), yield 0.4 g. Mixed m. p. of this compound

remain undepressed by admixture with the sample obtained by above procedure. (Found : C, 77.29; H, 4.4.  $C_{17}H_{12}O_3$  requires C, 77.27; H, 4.55%).

**6-Hydroxy-1,2,3,4-tetrahydroxanthone (Id) :**

A mixture of resorcinol (3 g) and ethyl cyclohexanone-2-carboxylate (4 ml) was refluxed with diphenyl ether (10 ml) for 3 hr. with a short condenser to facilitate the removal of alcohol formed. After cooling, the separated product was filtered and washed several times with petroleum ether. It crystallised from alcohol. M.P. 278°, yield 2.0 g. (Found : C, 72.38; H, 5.79.  $C_{13}H_{12}O_5$  requires C, 72.21, H, 5.55%).

**6-Allyloxy-1,2,3,4-tetrahydroxanthone (Ie) :**

A mixture of 6-hydroxy-1,2,3,4-tetrahydroxanthone (2 g), allylbromide (1 g) and anhydrous potassium carbonate (8 g) was refluxed in dry acetone (200 ml) in a water bath for 10 hr. The reaction mixture was worked up as described above, the product crystallised from petroleum ether, m.p. 88°, yield 1.5 g. (Found : C, 74.98; H, 6.24.  $C_{16}H_{16}O_5$  requires C, 75.00; H, 6.25%).

**5-Allyl-6-hydroxy-1,2,3,4-tetrahydroxanthone (If) :**

6-Allyloxy-1,2,3,4-tetrahydroxanthone (2 g) was refluxed with dimethyl aniline for 8 hr. The reaction mixture was worked up as described above. The product crystallised from alcohol, m.p. 236°, yield 1.5 g. (Found : C, 74.54; H, 6.47.  $C_{16}H_{16}O_5$  requires C, 75.00; H, 6.25%).

**5'-Methyl-1,2,3,4,4',5'-hexanhydrofurano (3',2',5,6)xanthone (IV) :**

5-Allyl-6-hydroxy-1,2,3,4-tetrahydroxanthone (1 g) was triturated with conc. sulphuric acid (5 ml) in a water bath for 15 minutes. The reaction mixture was worked up as described earlier. It crystallised from alcohol, m.p. 180°, yield 0.8 g. (Found : C, 75.23; H, 6.40.  $C_{16}H_{16}O_5$  requires C, 75.00; H, 6.25%). IR spectrum :  $1635\text{ cm}^{-1}$  ( $\gamma$ -pyronyl  $>C=O$  group).  $\lambda_{\text{max}}^{\text{Methanol}}$  248 nm (log e. 4.32), 255 nm (log e 4.35), 302 nm (log e 4.12).

**5'-Methylfurano (2',3'-3,4)xanthone (V) :**

A mixture of 5'-methyl-1,2,3,4,4',5'-hexanhydrofurano (3',2'-5,6) xanthone (0.5 g), palladised charcoal (10%, 0.3 g) and diphenyl ether (4 ml) was refluxed for 10 hr. The reaction mixture was worked up as described before. The product chromatographed on alumina. Elution with benzene-petroleum ether (1 : 1) gave 5'-methylfurano (2',3'-3,4)-xanthone (V) crystallised from alcohol and also from benzene-petroleum ether, m.p. 172° (lit<sup>9</sup>, m.p. 170°), yield 0.3 g. (Found : C, 76.81; H, 3.95.  $C_{16}H_{10}O_5$  requires C, 76.80; H, 4.00%). IR spectrum :  $1645\text{ cm}^{-1}$  ( $\gamma$ -pyronyl  $C=O$  group),  $825\text{ cm}^{-1}$  (furan ring).

**3-Allyloxyxanthone (VIc) :**

A mixture of 3-hydroxyxanthone (2 g), allyl-bromide (1.6 g) and anhydrous potassium carbonate (8 g) was refluxed in dry acetone (200 ml.) in a water bath for 14 hr. The reaction mixture was worked up as described above. The product crystallised from benzene-petroleum ether, m.p. 136° (lit<sup>9</sup>, m.p. 137°), yield 2.4 g. (Found : C, 75.69 ; H, 4.53. C<sub>16</sub>H<sub>12</sub>O<sub>3</sub> requires C, 76.19 ; H, 4.76%).

**4-Allyl-3-hydroxyxanthone (VIId) :**

3-Allyloxyxanthone (2 g) was refluxed with dimethylaniline (10 ml) for 5 hr. The reaction mixture was worked up as described before. The product crystallised from alcohol, m.p. 240° (lit<sup>9</sup>, m.p. 253°), yield 1.8 g. (Found : C, 75.78 ; H, 4.76. C<sub>16</sub>H<sub>12</sub>O<sub>3</sub> requires C, 76.19 ; H, 4.76%). IR spectrum : 1632 cm<sup>-1</sup> ( $\gamma$ -pyronyl >C=O group). and a broad band at 3150 cm<sup>-1</sup> (aromatic -OH group).

**4',5'-Dihydro-5'-methylfurano (2',3'-3,4)xanthone (VIII) :**

4-Allyl-3-hydroxyxanthone (1 g) was triturated with sulphuric acid (85%, 6 ml) in a water bath for 15 minutes. The reaction mixture was worked up as described above. It crystallised from alcohol and benzene-petroleum ether, m.p. 181° (lit<sup>9</sup>, m.p. 180°), yield 0.8 g. (Found : C, 76.40 ; H, 4.66. C<sub>16</sub>H<sub>12</sub>O<sub>3</sub> requires C, 76.19 ; H, 4.76%). NMR (CDCl<sub>3</sub>) :  $\delta$ 1.54 (3H, d, J=7Hz, C5'-CH<sub>3</sub>), 2.80-3.62 (2H, m, C<sub>4</sub>'-H<sub>2</sub>), 5.15 (1H, q, J=7Hz, C5'-H), 6.7 (1H, d, J=9Hz, C<sub>2</sub>-H), 7.2-7.7 (3H, m, C<sub>6</sub>-H, C<sub>8</sub>-H and C<sub>7</sub>-H), 8.06 (1H, d, J=9Hz, C<sub>1</sub>-H), 8.25 (1H, d, J=9Hz, C<sub>8</sub>-H).

**5'-Methylfurano (2',3'-3,4)xanthone (V) :**

A mixture of 4',5'-dihydro-5'-methylfurano (2',3'-3,4)xanthone (0.5 g), palladised charcoal (10%, 0.3 g) and diphenyl ether (4 ml) was refluxed for 12 hr. The reaction mixture was worked up as described before. The product chromatographed on alumina. Elution with benzene-petroleum ether (3 : 7) gave the product, which crystallised from

alcohol, m.p. 172° (lit<sup>9</sup>, m.p. 170°), yield 0.3 g. Mixed m.p. with the compound obtained as above was not depressed. (Found : C, 76.37 ; H, 3.87. C<sub>16</sub>H<sub>10</sub>O<sub>3</sub> requires C, 76.81 ; H, 4.00%).

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