SUMMARY

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Xanthones form a class of oxygen heterocycles and are compounds of interest as they occur in nature. Some of the natural occuraing xanthones and synthetic xanthones have been found to possess various pharmacological properties.

The present work deals with the synthesis of xanthones adopting a new single step method for the synthesis of xanthones, bromination study of various hydroxyxanthones, and syntheses of furanoxanthones, syntheses of pyranoxanthones.

Chapter I is introduction to the naturally occuring xanthones and their physiological properties.

Chapter II
Syntheses of xanthones

For preparing any synthetic xanthone of pharmacological interest basic thing is to obtain simple type of xanthone in good yield. In the present investigation variety of xanthones have, therefore, been prepared in good yields by the thermal condensation of substituted phenols with substituted ethyl or methyl salicylates derivatives in diphenylether, without using any condensing agent. Phenols such as phloroglucinol, resorcinol,

2-methylresorcinol, 5-methylresorcinol, pyrogallol, α-naphthol and β-naphthol, when condensed with methyl-2,6-dihydroxybenzoate, methyl 2,4-dihydroxybenzoate give corresponding xanthone derivatives.

Naturally occuring xanthones viz 2-hydroxyxanthone, 2-methoxyxanthone, 1,7-dihydroxyxanthone, 1,5-dihydroxy xanthone, 2,6-dihydroxyxanthone, 1,5,6-trihydroxyxanthone, and 1,3,7-trihydroxyxanthone have been achieved in good yield.

In the condensation of hydroquinone with ethyl salicylate, six products were obtained each of them were characterised on the basis of spectral studies.

Condensation of other methyl salicylates, bearing hetrocylic system on it, with reactive phenol, viz. phloroglucinol, gave xanthone derivatives.

The structures of the condensation products were confirmed by preparing acetates or methyl ether derivatives and also by spectral data.

Chapter III

Bromination of xanthones

A survey of the literature reveals that few bromo xanthones possess insecticidal activity. It was, therefore, considered thought of interest to investigate the bromination of xanthones and to test the insecticidal and Herbicidal properties of bromoxanthones.

Bromination of 3-hydroxy-, 2-hydroxy-, 1-hydroxy-3-methyl-, 3-hydroxy-4-methyl-, 1-hydroxy-, and 7-bromo-3-hydroxyxanthone has been carried out using bromine in acetic acid as a brominating agent to get dibromo derivatives of xanthone. Same reagent failed to give mono bromo derivatives even in mild conditions. Mono bromoxanthone were prepared by using pyridine hydrobromine perbromide as a brominating agent, for the first time. The structure of mono and dibromo hydroxy xanthones were confirmed by elemental analysis, IR, NMR and Mass spectral studies.

Chapter IV

Synthesis of Furanoxanthones

3-hydroxy-4-bromoxanthone and 2,4-dibromo-3-hydroxy xanthone on allylation with allyl bromide in presence of anhydrous potassium carbonate in dry acetone gave 3-allyloxy-4-bromoxanthone and 2,4-dibromo-3-allyloxy xanthone which on Claisen migration in dimethyl aniline gave corresponding hydroxy allylxanthone and dihydro furanoxanthone. Claisen migration of above allyloxy compound has also been studied in other inert solvent like dekalin and also by prolysis in vacuum. Claisen migration of 2,4-dibromo-3-allyloxyxanthone under vacuum gave abnormal products.

4-bromo-2-allyl-3-hydroxyxanthone on treatment with Osmium tetroxide and potassium periodate followed by cyclisation in PPA furnished 4-bromo-furano (2',3'-2,3) xanthone 4-bromo-2-allyl-3-acetoxyxanthone on bromination, followed by refluxing in alcoholic KOH, gave 4-bromo-5'-methylfurano (3',2'-2,3) xanthone.

Similarly 2-bromo-5'-methylfurano (2',3',3,4) xanthone and 2-bromofurano (2',3':3,4)xanthone were synthesised from 2-bromo-4-allyl-3-hydroxyxanthone.

Also starting from 1,6-dihydroxy-3-methyl and 3-6 dihydroxyxanthone mono and difuranoxanthone have also been synthesised by the method used by Rindfusz and Adams for the synthesis of furanocompounds.

3-hydroxy-4-bromo-, 2,4-dibromo-3-hydroxy-, 1-hydroxy-2-bromo-3-methyl-, 1-bromo-2-hydroxyxanthone and 2-bromo-1-hydroxyxanthone was coupled with cuprous phenylacetylide in pyridine under nitrogen atmosphere, following furanoxanthones are synthesised:

1) 5'-Phenyl furano (2',3':3,4)xanthone
2) 2-bromo 5'-phenylfurano (2',3':3,4)xanthone
3) 5'-phenyl furano (2',3':3,4)xanthone
4) 5'-phenyl furano (3',2':1,2)xanthone
5) 5'-phenyl-3-methylfurano (2',3':1,2)xanthone

Coupling of cuprous salt of THP ether of 3-hydroxy-3-methyl-but-1-yne with 3-acetoxy-4-bromo, 2-bromo-3-hydroxy-4, methyl-, 1-bromo-2-hydroxyxanthone in pyridine under nitrogen atmosphere gave following furanoxanthones:

1) 5'-(1-hydroxy-1-methylethyl)Furano (2',3':3,4)xanthone
2) 5'-(1-hydroxy-1-methylethyl)Furano (3',2':1,2)xanthone
3) 5'-isopropenyl-4-methyl Furano (3',2':2,3)xanthone

3-Hydroxy-, 2-hydroxy-, 1-hydroxy-3-methyl xanthone on cinnamylation followed by claisen migration in N,N-dimethylaniline gave ortho hydroxy cinnamylxanthone and methyl-5'-phenyl-4',5'-dihydrofuranoxanthones, the latter one when refluxed with pd/c in diphenyl ether furnished the following furanoxanthones:

1) 5'-methyl-4'-phenyl furano (2',3':3,4)xanthone
2) 5'-methyl-4'-phenyl furano (3',2':1,2)xanthone
3) 3,5'-dimethyl-4'-phenyl furano (2',3':1,2)xanthone

The structures of intermediate and furanoxanthone were established by their NMR spectral data.

Chapter V

Synthesis of pyranoxanthones

A Claisen rearrangements of 3-prenyloxy-, 2-prenyloxy-, 3-prenyloxy-4-methyl-, 3-prenyloxy-4-bromo-, and 3-prenyloxy-4-iodoxanthone have been studied in different solvents and in vacuum. In almost all the cases abnormal claisen migration products were obtained.

3-Hydroxyxanthone with BF_3 Etherate, and prenyl alcohol in dioxan gave 6',6'-dimethyl 4',5'-dihydro pyrano (2',3':3,4)xanthone. 3-Hydroxyxanthone was alkylated with 3-chloro-3-methyl but-1-yne in presence of K_2CO_3 and dry acetone and the product obtained was subjected to claisen rearrangement in N,N-dimethyl aniline to obtain 6',6'-dimethyl pyrano (2',3':3,4) xanthone.

6',6'-Dimethyl-1,3-dihydroxy-4',5'-dihydro pyrano (2',3'-6,7)xanthone and 1,3,8-trihydroxy-6',6'-dimethyl-4',5'-dihydro pyrano (2',3':5,6) xanthone were synthesised by condensation of phloroglucinol with substituted methyl salicylate derivatives.

A novel observation on the Claisen rearrangement of 2,4-dibromo-3-allyloxyxanthone

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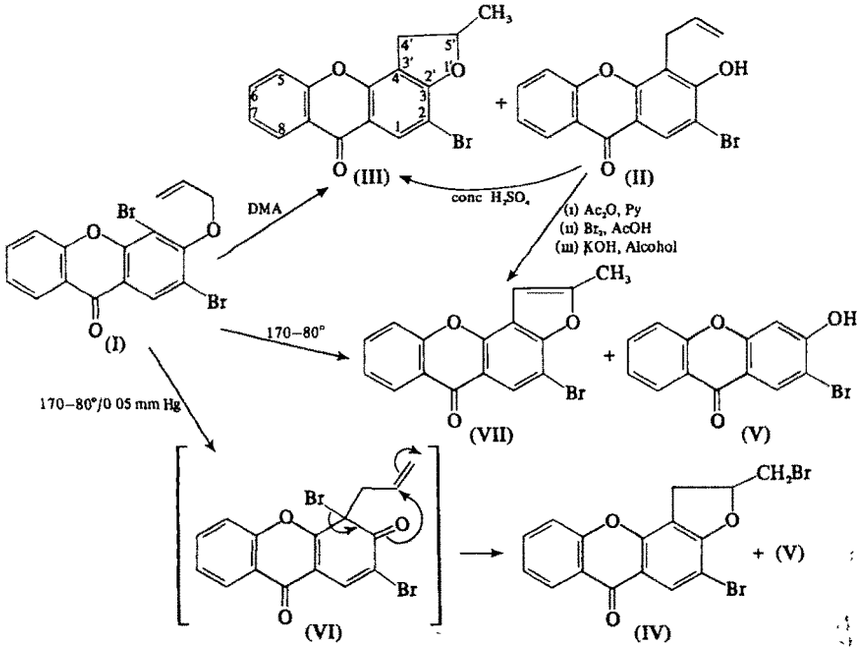
Claisen rearrangement of 2,4-dibromo-3-allyloxyxanthone (I) in *N,N*-dimethylaniline yielded two products, 2-bromo-3-hydroxy-4-allylxanthone (II), mp 197°C; *m/e* 332, 330 (M^+), 304, 302 (M^+-CO), 250 (M^+-Br); n.m.r. ($CDCl_3$): δ 3.75(*d*, 2H, J = 5Hz, $-CH_2CH=CH_2$), 5.1(*m*, 2H, $-CH_2CH=CH_2$), 6.0(*m*, 1H, $-CH_2CH=CH_2$), 7.35 (*td*, 1H, J = 8,8,2Hz, H-7), 7.49(*d*, 1H, J = 9Hz, H-5), 7.7(*td*, 1H, J = 8,8,2Hz, H-6), 8.3(*d*, 1H, J = 9Hz, H-8), 8.4(*s*, 1H, H-1) and 2-bromo-4′,5′-dihydro-5′-methylfurano(2′,3′:3,4)xanthone (III), mp 187°C; *m/e* 332, 330 (M^+), 304, 302 (M^+-CO); n.m.r. ($CDCl_3$): δ 1.7(*d*, 1H, J = 7Hz, (5′-CH_3), 3.1(*q*, 1H, J = 18Hz, 4′-H), 3.6 (*q*, 1H, J=18Hz, 4′-H), 5.25(*m*, 1H, 5′-H), 7.35-7.65(*m*, 3H, ArH), 8.25(*s*, 1H, H-1), 8.25(*d*, 1H, J = 9Hz, H-8). Compound (III) was also obtained when compound (II) was cyclised with conc. sulphuric acid.[1]

Claisen rearrangement of compound (I) under reduced pressure (0.05mm) at 170-80°C for 4h also gave two products, 2-bromo-5′-bromomethyl-4′,5′-dihydrofurano (2′,3′:3,4)xanthone (IV), mp 187-250°C; *m/e* 412, 410, 408 (M^+), 332, 330 (M^+-Br); n.m.r. ($CDCl_3$): δ3.4(*d*, 2H, 4′-H_2), 3.65(*m*, 2H, $-CH_2Br$), 5.3(*m*, 1H, 5′-H), 7.23(*td*, 1H, J = 9,9,2Hz, H-7), 7.35(*d*, 1H, J = 9Hz, H-5), 7.63(*td*, 1H, J = 9,9,2Hz, H-6), 8.2(*dd*, 1H, J = 9,2Hz, H-8), 8.22(*s*, 1H, H-1) and 2-bromo-3-hydroxyxanthone (V), mp 310°C; *m/e* 292, 290 (M^+), 264, 262 (M^+-CO), 235, 233,



($M^+ - CO\text{-}CHO$); n.m.r. ($CDCl_3$): δ7.02(*s*, 1H, H-4), 7.4(*td*, 1H, J = 8,8,2Hz, H-7), 7.52(*d*, 1H, J = 8Hz, H-5), 7.77(*td*, 1H, J = 8,8,2Hz, H-6), 8.15(*dd*, 1H, J = 8,2Hz, H-8), 8.23(*s*, 1H, H-1), 11.5(*s*, 1H, OH exchangeable with D_2O). Formation of compound (IV) can be explained by thermally-favourable [1,3] sigmatropic rearrangement of compound (I) to give a ketonic intermediate (VI) which undergoes cyclisation involving bromine to afford the product (IV). The formation of compound (IV) is a novel observation in the Claisen rearrangement. Compound (I), on heating at 170-80°C for 4h gave compound (V) and 2-bromo-5′-methylfurano(2′,3′:3,4)xanthone (VII), mp 235°C; *m/e* 330, 328 (M^+), 302, 300 ($M^+ - CO$); n.m.r. ($CDCl_3$): δ2.55(*s*, 3H, 5′-CH_3), 6.82(*s*, 1H, 4′-H), 7.4(*td*, 1H, J = 9,9,2Hz, H-7), 7.5(*d*, 1H, J = 9Hz, H-5), 7.76(*td*, 1H, J = 9,9,2Hz, H-6), 8.30(*s*, 1H, H-1), 8.32(*dd*, 1H, J = 9,2Hz, H-8). Compound (VII) was identical (n.m.r. and mass spectra, t.l.c.) with 2-bromo-5′-methylfurano (2′,3′:3,4)xanthone prepared from (II) by the method of Adams and Rindfusz.[2]

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Studies in Synthesis of Xanthones: Part IV†—Synthesis of Furanoxanthones

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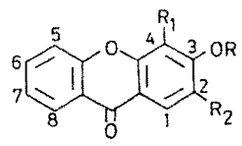
The Claisen migrations of 3-allyloxy-4-bromoxanthone and 3-allyloxy-4-iodoxanthone have been carried out in dimethylaniline, decalin and *in vacuo* to obtain different xanthones 4-Bromofurano[3', 2':2, 3]xanthone (X) and 4-bromo-5'-methylfurano[3', 2':2, 3]xanthone (IX), have been synthesised from 2-allyl-3-hydroxy-4-bromoxanthone (VII) The structures of intermediates and final products have been confirmed by IR, mass and PMR spectral studies

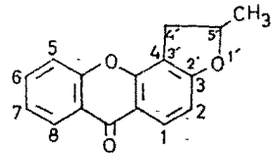
In an earlier paper, we reported the synthesis of linear furanoxanthones involving Claisen migration of 3-allyloxy-4-methylxanthone[1]. During our work on the synthesis of psoralene derivatives[2,3], it was observed that when 8-position of coumarin ring was blocked by bromine, subsequent Claisen rearrangement, for example, of 7-allyloxy-8-bromocoumarin in dimethylaniline gave 7-hydroxy-6-allylcoumarin, bromine being eliminated during migration. We have extended this work to the bromoallyloxyxanthone derivatives and report herein the synthesis of linear furanoxanthones (IX) and (X).

Bromination of 3-hydroxyxanthone using pyridine hydrobromide perbromide[4] in acetic acid gave 4-bromo-3-hydroxyxanthone (I) Its structure was established on IR, PMR and mass spectra of the corresponding acetate derivative (see Experimental). I on treatment with allylbromide afforded the corresponding 3-allyloxy-4-bromoxanthone (II).

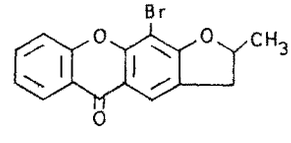
Claisen migration of II and 3-allyloxy-4-iodoxanthone (III), prepared by the allylation of the known 3-hydroxy-4-iodoxanthone[5], in dimethylaniline gave 2-allyl-3-hydroxyxanthone (IV), 4-allyl-3-hydroxyxanthone (V) and 5'-methyl-4', 5'-dihydrofurano[2', 3':3, 4]xanthone (VI). One-proton singlets at δ 6.8 and 7.85 in the PMR spectrum of IV and assignable to H-1 and H-4 respectively revealed the migration of allyl group to position-2. That VI is an angular furanoxanthone was proved by its PMR spectrum which displayed two one-proton doublets at δ 8.12 (J=9 Hz, H-1) and 7.75 (J=9 Hz, H-2) indicating that it is an angular furanoxanthone. III when refluxed in decalin gave 3-allyloxyxanthone, iodine being eliminated during the reaction. While II in refluxing decalin gave 2-allyl-3-hydroxy-4-bromoxanthone (VII), V and VI. Structure of VII was confirmed by the PMR spectrum of its acetoxy derivative which exhibited a one-proton singlet at δ 8.18, characteristic of proton H-1 and no other singlet in aromatic region, indicating the migration of allyl group to position-2; bromine was not eliminated during the reaction. When the rearrangement was carried out *in vacuo* at 140-50°, II furnished the compounds (V-VII), however, in poor yield. III when heated *in vacuo* at 140-50° gave 3-allyloxyxanthone and V. During the migration of III in dimethylaniline *p*-iodo-N, N-dimethylaniline (M^+ 247) was isolated.



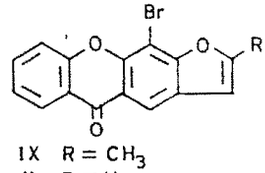
	R	R_1	R_2
I	H	Br	H
II	$CH_2CH=CH_2$	Br	H
III	$CH_2CH=CH_2$	I	H
IV	H	H	$CH_2CH=CH_2$
V	H	$CH_2CH=CH_2$	H
VII	H	Br	$CH_2CH=CH_2$
VIII	$OCOCH_3$	Br	$CH_2CHBrCH_2Br$



VI



XI



IX R = CH_3
X R = H

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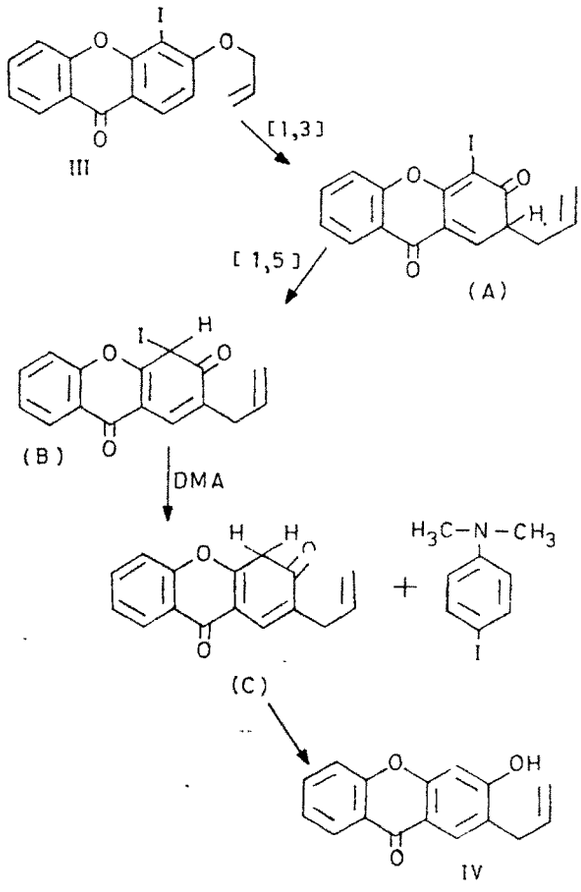

Scheme 1

The mechanism shown in Scheme 1 is proposed to explain the formation of IV. In the first step [1, 3]sigmatropic rearrangement occurs to give the ketonic structure (A) and in the second step [1, 5] hydrogen shift in (A) gives rise to structure (B), which can easily liberate iodine to displace a proton from dimethylaniline, to form *p*-iodo-N, N-dimethylaniline and (C). The intermediate (C) undergoes keto-enol tautomerism to give the stable phenol (IV).

Using Adams and Rindfusz[6] method for developing furan ring, VII was converted into 4-bromo-5'-methylfurano [3', 2':2, 3]xanthone (IX) VII on treatment with osmium tetroxide and potassium periodate followed by cyclisation with PPA gave 4-bromofurano[3', 2':2, 3]xanthone (X).

Experimental Procedure

The reported m.ps are uncorrected PMR spectra were recorded on Perkin-Elmer R 34 (220 MHz) and Perkin-Elmer R 32 (90 MHz) instruments using TMS as an internal standard. IR spectra (ν_{max} in cm^{-1}) were recorded on a Perkin-Elmer 125 spectrophotometer and mass spectra on an AEI MS12 machine.

3-Hydroxy-4-bromoxanthone (I)

To 3-hydroxyxanthone (2 g) dissolved in glacial acetic acid (80 ml) and warmed to 55° was added pyridine hydrobromide perbromide (3.2 g). The reaction mixture was stirred for 30 min diluted with water the solid obtained filtered off and crystallised from ethyl acetate to give I as brown needles (1.8 g), m.p. 254° (Found: C, 53.3; H, 2.5 $C_{13}H_7O_3Br$ requires C, 53.8; H, 2.4%), acetate (Ac_2O/C_5H_5N), m.p. 181° (Found: C, 54.2, H, 2.9. $C_{15}H_9O_4Br$ requires, C, 54.4; H, 2.7%). MS: *m/z* 334, 332, 292, 290, (100), 264, 262, 235, 233, 221, 212, 183, 155, 127, 126, 121, 87, 78, 58, 43. PMR ($CDCl_3$): δ 8.35 (*d*, 1H, J=9 Hz, H-1), 7.18 (*d*, 1H, J=9 Hz, H-2), 7.57 (*d*, 1H, J=9 Hz, H-5), 7.75 (*td*, J=9, 9, 2 Hz, H-6), 7.4 (*td*, 1H, J=9, 9, 2 Hz, H-7), 8.30 (*dd*, 1H, J=9, 2 Hz, H-8), 2.4 (*s*, 3H, $-COCH_3$).

3-Allyloxy-4-bromoxanthone (II)

A mixture of above compound (10 g) allyl bromide (7 ml) and anhydrous potassium carbonate (10 g) was refluxed in dry acetone (200 ml) on a water-bath for 12 hr. The reaction mixture was poured into water, the solid filtered off, washed with dil. aq. sodium hydroxide, and crystallised from aq. ethanol to give II as light yellow needles (5 g), m.p. 121° (Found: C, 58.3; H, 3.8. $C_{16}H_{11}O_3Br$ requires C, 58.2; H, 3.3%).

3-Allyloxy-4-iodoxanthone (III)

Allylation of 3-hydroxy-4-iodoxanthone[5] (reflux 20 hr), similar to that adopted in the case II, furnished III which crystallised from ethyl acetate as pale yellow needles (3 g), m.p. 142° (Found: C, 50.4; H, 3.4. $C_{16}H_{11}O_3I$ requires C, 50.8; H, 2.9%).

Claisen migration of 3-allyloxy-4-bromoxanthone

(a) In DMA—II (10 g) was refluxed with dimethylaniline (25 ml) for 8 hr. After cooling, the reaction mixture was poured into cold dil. hydrochloric acid, separated solid filtered and stirred with aq. sodium hydroxide and filtered again. Solid obtained was crystallised from ethyl acetate to give the furanoxanthone VI as white needles (0.2 g), m.p. 180° (lit.[7] 180°; lit.[1] 181°) (Found: C, 75.8; H, 4.7. Calc. for $C_{16}H_{12}O_3$: C, 76.2, H, 4.7%); IR (KBr): 1645 (C=O, γ-pyronyl); MS: *m/z* 252, 237, 225, 212, 209, 197, 181, 168, 165, 152, 139, 126, 115, 105, 92, 87, 77, 63; PMR ($CDCl_3$): δ 8.12 (*d*, 1H, J=9 Hz, H-1), 7.76 (*d*, 1H, J=9 Hz, H-2), 7.36 (*d*, 1H, J= 9Hz, H-5), 7.6 (*td*, 1H, J=8, 8, 2 Hz, H-6), 7.3 (*td*, 1H, J=8, 8, 2Hz, H-7), 8.3 (*d*, 1H, J=9 Hz, H-8), 5.15 (*m*, 1H, H-5'), 3.6 (*q*, 1H, J=18 Hz, H-4'), 2.95 (*q*, 1H, J=18 Hz, H-4'), 1.5 (*d*, 3H, J=7 Hz, C_5-CH_3).

The filtrate on acidification with concentrated hydrochloric acid gave a solid (2 g) which showed two

spots on TLC (chloroform-methanol, 40:1) R_f 0.77, 0.45. The crude product was chromatographed over silica gel using benzene and then subjected to preparative TLC (chloroform-methanol, 40:1) to furnish 2-allyl-3-hydroxyxanthone (IV) (50 mg) as white seeds from ethanol, m.p. 233° (Found: C, 75.7; H, 4.5. $C_{16}H_{12}O_3$ requires C, 76.2, H, 4.8%). MS: *m/z* 252, 237, 235, 224, 209, 205, 197, 181, 165, 152, 139, 121, 115, 102, 92, 87, 77, 63, 50; PMR (CD_3SOCD_3). δ 7.85 (*s*, 1H, H-1), 6.8 (*s*, 1H, H-4), 7.58 (*d*, 1H, J=9 Hz, H-5), 7.68 (*td*, 1H, J=9, 9, 2 Hz, H-6), 7.4 (*td*, 1H, J=9, 9, 2 Hz, H-7), 8.13 (*dd*, 1H, J=9, 2 Hz, H-8), 6.0 (*m*, 1H, $CH_2CH=CH_2$), 5.15 (*m*, 2H, $-CH_2CH=CH_2$), 3.38 (*d*, 2H, J=7 Hz, $-CH_2CH=CH_2$). 4-Allyl-3-hydroxyxanthone (V) (120 mg) crystallised from aq. ethanol, m.p 245 (lit.[7] 253, lit.[1] 240); MS. *m/z* 252, 237, 236, 225, 212, 209, 208, 197, 184, 181, 168, 152, 141, 139, 121, 115, 102, 92, 82, 77, 65; PMR (CD_3SOCD_3): δ 7.99 (*d*, 1H, J=8.5 Hz, H-1), 7.4 (*d*, 1H, J=8.5 Hz, H-2), 7.58 (*d*, 1H, J=8 Hz, H-5), 7.78 (*td*, 1H, J=8, 8, 2 Hz, H-6), 7.41 (*td*, 1H, J=8, 8, 2 Hz, H-7), 8.17 (*dd*, 1H, J=8, 2 Hz, H-8), 6.0 (*m*, 1H, $-CH_2CH=CH_2$), 5.11 (*m*, 2H, $-CH_2CH=CH_2$), 3.62 (*d*, 1H, J=7 Hz, $-CH_2CH=CH_2$). Further elution with chloroform gave 4-allyl-3-hydroxyxanthone (V).

(b) In decalin—3-Allyloxy-4-bromoxanthone (II, 7 g) was refluxed with decalin (35 ml) for 3 hr. After cooling, the separated solid was filtered off, dissolved in aqueous sodium hydroxide solution and again filtered. The filtrate on acidification with conc. hydrochloric acid gave the product (1.7 g) which showed two spots on TLC (chloroform-methanol, 40:1). R_f 0.07, 0.45. The product was chromatographed over silica gel. Elution with benzene gave 2-allyl-4-bromo-3-hydroxyxanthone (VII) (400 mg), m.p. 167° (Found: C, 58.4, H, 3.5. $C_{16}H_{11}O_3Br$ requires C, 58.2; H, 3.0%); acetate (Ac_2O/C_5H_5N), m.p. 140°; IR (KBr): 1760 (C=O, ester), 1670 (>C=O, γ-pyronyl). MS: *m/z* 374, 372, 332, 330 (100), 318, 303, 301, 292, 290, 252, 251, 250, 236, 223, 222, 221, 205, 196, 195, 176, 166, 152, 139, 121, 102, 100, 92, 91, 87, 81, 63; PMR ($CDCl_3$): δ 8.13 (*s*, 1H, H-1), 7.5 (*d*, 1H, J=9 Hz; H-5), 7.7 (*td*, 1h, J=8, 8, 2 Hz, H-6), 7.35 (*td*, 1H, J=8, 8, 2 Hz, H-6), 7.35 (*td*, 1H, J=8, 8, 2 Hz, H-7), 8.28 (*dd*, 1H, J=9 Hz, H-8), 2.4 (*s*, 3H, $OCOCH_3$), 5.9 (*m*, 1H, $CH_2CH=CH_2$), 5.15 (*m*, 2H, $-CH_2CH=CH_2$), 3.4 (*d*, 2H, J=5 Hz, $CH_2CH=CH_2$). Further elution with chloroform gave 4-allyl-3-hydroxyxanthone (V) (1.2 g).

In vacuo

3-Allyloxy-4-bromoxanthone (II, 2 g) was heated *in vacuo* at 140-50° for 5 hr. The product was extracted with acetone, acetone distilled off, residue dissolved in aq. sodium hydroxide, and filtered. The filtrate on acidification with conc. hydrochloric acid gave the product which showed the spotting pattern on TLC as was shown by the product obtained by carrying out the rearrangement in decalin. Alkali insoluble portion gave starting material and cyclised product (VI).

4-Bromo-4',5'-dihydro-5-methylfurano [3',2':2,3]xanthone (XI)

VII (200 mg) was triturated with conc. sulphuric acid[8] on a water-bath for 15 min. The contents were poured on to crushed ice, the separated product was filtered and washed with dil. aq. sodium hydroxide solution to remove uncyclised compound. The solid was crystallised from benzene-ethanol (50:50) to give XI as yellow needles, m.p. 190° (120 mg) (Found: C, 57.7; H, 3.2. $C_{16}H_{11}O_3Br$ requires C, 58.2, H, 3.0%); PMR ($CDCl_3$): δ 8.12 (*s*, 1H, H-1), 8.02 (*d*, 1H, J=9 Hz, H-8), 7.0-7.6 (*m*, 4H, ArH), 5.1 (*m*, 1H, C_5-H), 3.45 (*q*, 1H, J=18 Hz, C_4-H), 3.29 (*q*, 1H, J=18 Hz, C_4-H), 1.35 (*d*, 1H, J=7 Hz, C_5-CH_3).

4-Bromofurano [3',2':2.3]xanthone (X)

2-Allyl-4-bromo-3-hydroxyxanthone (1 g) in ethyl acetate (100 ml) and osmium tetroxide (1 g) in water (60 ml) were vigorously stirred for 15 min. Potassium periodate (2 g) was added in small quantities to the dark black solution during 2 hr. The reaction mixture was stirred for further 4 hr. The ethyl acetate layer separated, washed with water, dried (Na_2SO_4) and the solvent removed. The residue was crystallised from ethanol or benzene-petroleum ether, m.p. 200° (650 mg) (Found: C, 53.6; H, 3.1. $C_{15}H_9O_4Br$ requires C, 54.1; H, 2.7%).

The above product was taken in PPA (10 g), heated in an oil-bath for 2 hr at 115° and poured over crushed ice. The separated solid was washed with dil. aq. sodium hydroxide and extracted with benzene-ethanol. This solution was percolated through a column of silica gel and eluted with benzene-ethanol (50:50) to afford X as a solid (80 mg) which crystallised from benzene, as yellow needles, m.p. 240° (Found: C, 57.6; H, 2.5. $C_{15}H_7O_3Br$ requires C, 57.2; H, 2.2%). IR (KBr): 1670 (>C=O γ-pyronyl), 1620 cm^{-1} (C=C), MS: *m/z* 316, 314 (100), 288, 286, 284, 256, 236, 235, 207, 179, 151, 150, 143, 126, 92, 88, 77, 63, 43; PMR ($CDCl_3$): δ 8.55 (*s*, 1H, H-1), 7.45 (*d*, 1H, J=9 Hz, H-5), 7.75 (*td*, 1H, J=9, 9, 2 Hz, H-6), 7.7 (*td*, 1H, J=9, 9, 2 Hz, H-7), 8.33 (*dd*, 1H, J=8, 2 Hz, H-8), 7.7 (*d*, 1H, J=1, 5 Hz, C_5-H), 6.99 (*d*, 1H, J=1.5 Hz, C_4-H).

2-(2',3'-Dibromopronyl)-3-acetoxy-4-bromoxanthone (VIII)

2-Allyl-3-acetoxy-4-bromoxanthone (180 mg) was dissolved in acetic acid (30 ml). To this bromine in glacial acetic acid (5 ml, 1% v/v) was added and the

reaction mixture stirred for 2 hr and poured into water The separated solid was crystallised from aq. ethanol or acetic acid. m.p. 170° (180 mg) MS· *m/z* 534, 532, 494, 492, 490, 488, 413, 411, 409, 332, 330, 305, 303 (100), 250, 223, 196, 165, 139, 121, 102, 92, 82, 43

4-Bromo-5'-methylfurano[3',2':2,3]-*xanthone* (*IX*)

X (150 mg) was refluxed in alc. potassium hydroxide (10%, 40 ml) for 8 hr and poured into water The separated product was washed with dil. aq. sodium hydroxide and crystallised from ethanol-benzene to give IX as white needles (50 mg), m p 243-45 (Found. C, 59.0; H, 2.9 $C_{16}H_9O_3Br$ requires: C, 58 5; H, 2.7%), PMR ($CDCl_3$): δ 8.28 (*s*, 1H, H-1), 8 23 (*d*, 1H, *J* =9 Hz, H-8), 7.28 to 7.6 (*m*, 3H, ArH), 6.5 (*s*, 1H, C_4-H), 2.5 (*s*, 3H, CH_3).

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