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9*H*-Xanthen-9-ones from 4*H*-1-benzopyran-4-ones†

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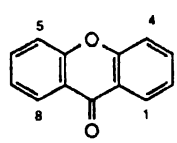
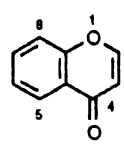
An account of the synthesis of 9*H*-xanthen-9-ones (xanthones) by incorporating 1-4 carbon components into the appropriate 4*H*-1-benzopyran-4-ones (chromones) mainly through either a proper cycloaddition or Michael Initiated Ring Closure reaction as well as by [6+0]cyclisation of the appropriately substituted chromones is presented.

The compounds containing the 9*H*-xanthen-9-one (trivial name : xanthone) moiety **A** or its reduced form are abundant in nature. Resurgent interest in xanthone is, however, due to successful synthesis of some xanthone-based analogues of the anthracycline antitumour agents and the antibiotic bikaverin having a benzo[*b*]xanthone skeleton. The two most significant synthetic routes to xanthones basically involve ring closure on to either the oxygen atom or the carbonyl carbon atom of the appropriately substituted benzenes[1]. The recent trend to construct xanthones from the compounds containing the 4*H*-1-benzopyran-4-one (trivial name : chromone) moiety **B** has, however, attracted much attention and an account of the same, with particular emphasis on the work reported from this laboratory, is presented in the following few sections and subsections based on the nature of the carbon components being annulated with the chromone derivatives and the types of the reactions invloved in such annulation processes. Alkyl, alkoxy and halogeno substituents in the benzene ring of the chromones remain unaffected in most of the reactions described here for the chromone with its unsubstituted benzene nucleus.



A



B

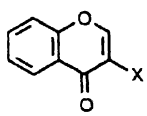
Annulation of four-carbon components with the 2,3-olefinic bond of chromones

Chromone **1** is benzannulated γ-pyrone and like γ-pyrone it is non-aromatic. The enone moiety of **1**, unless its dienophilicity is enhanced by the presence of a sufficiently electron-withdrawing group, fails to participate in Diels-Alder reaction[2]. As for example, 3-bromochromone is reactive only with 1,3-cyclohexadiene giving a stereoisomeric mixture of the corresponding [4+2]cycloadduct in less than 10% yield even after heating at 300° for 120 h[2]. The formation of the *cis*-adduct **12** (X = H, Me, CO_2Me) from each of the chromones **1**, **2** and **5** (R = Me) and the α,β-unsaturated ketone **9** [R^1 = H, Me, Et, R^2 = R^4 = H, R^5 = H, Me, Ph, R^4-R^5 = $(CH_2)_4$, R^6 = H, Me] in the presence of *t*-butyldimethylsilyl triflate and 2,6-lutidine is not regarded as a proper [4+2]cycloaddition reaction. The reaction is initiated by the attack of 2-silyloxybutadiene **10** [R^3 = $OSi(CMe_3)Me_2$], derived from **9** and silyl triflate, at 2-position of 4-*t*-butyldimethylsilyloxy-1-benzopyrilium triflate **11**[3,4]. Formation of the tetrahydroxanthone **12** (X = H or Me) from the diene **10** (R^1 = R^2 = R^5 = R^6 = H, R^3 = Me, R^4 = H or Me) and chromone **1** or **2** also involves a Michael Initiated Ring Closure (MIRC) mechanism[4]. Compound **12** (X = R^1 = R^2 = R^4-R^6 = H, R^3 = Me) on treatment with DDQ in the presence of *p*-TsOH is aromatised to 3-methylxanthone[4].

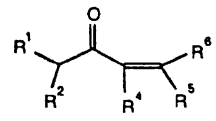
The 3-substituted chromones **3**, **4**, **5** (R = H, Me) and **6** undergo [4+2]cycloaddition with 2,3-dimethylbuta-1,3-diene under titanium tetrachloride catalysis and with highly electron-rich dienes without the assistance of any Lewis acid catalyst, the stability of the cycloadduct depending on the nature of the X group[2,5]. The adduct **12** [X = $S(O)C_6H_4Cl$-*p*, R^1 = R^2 = R^4 = R^5 = H, R^3 = $OSi(CMe_3)Me_2$, R^6 = OMe], derived from **6** and Danishefsky's diene, is prone to undergo aromatisation to 3-hydroxyxanthone **13** (R^1-R^3 = H) via *syn*-elimination of *p*-chlorobenzenesulphenic acid and 1,4-elimination of methanol[5]. The stereochemistry of [4+2]cycloaddition of 3-cyanochromone **3** with electron-rich dienes is influenced by the reaction concentrations of the former[6]. The adduct **12** (X = CN, R^1 = R^2 = R^4 = R^5 = H, R^3 = OSTB, R^6 = OMe, *exo* : *endo* ≈ 1 : 2), derived from **3** and Danishefsky's diene, is hydrolysed by TMSB in acetonitrile at room temperature to the enone **14** aromatisable to **13** (R^1-R^3 = H)[7]. High asymmetric induction has been achieved in the [4+2]cycloaddition of 3-alkoxycarbonylchromone (**5**, R containing a chiral centre) with Danishefsky's diene[8]. Synthesis of xanthones by react-

†Dedicated with profound respect and gratitude to Professor D. Nasipuri on his 75th. birth anniversary.

ing 3-substituted chromones with chromone based dienes is discussed later.



1 X = H
2 X = Me
3 X = CN
4 X = CHO
5 X = CO_2R
6 X = $S(O)C_6H_4Cl$-*p*
7 X = CH=CHCOMe (*trans*)
8 X = CH=CHC(=NOH)Me



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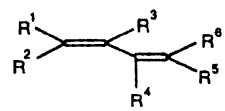

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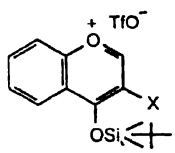

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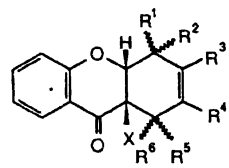

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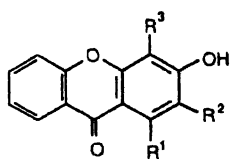

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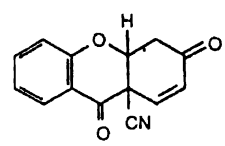

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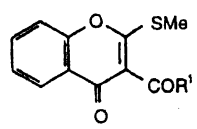

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Annulation of three-carbon components with the appropriate chromone derivatives

Base catalysed condensation of appropriate methylene compounds with 3-acyl-2-thiomethylchromone gives xanthones by a Michael addition – elimination – cyclisation sequence. As for example, **15** (R^1 = H, Me, Ph) in the presence of potassium *t*-butoxide gives **13** (R^2 = H, R^3 = Ac) with acetylacetone and **13** ($R^2 = R^3 = CO_2Et$) with diethyl α-ketoglutarate[9].

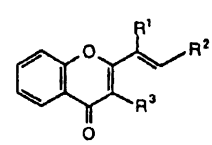
Annulation of two-carbon components with the appropriate chromone derivatives

Annulation involving an initial [4+2]- or [2+2]cycloaddition :

The pyran 2,3-olefinic bond becomes a part of the diene system in 2- and 3-ethenylchromones. Again, some 2,3-disubstituted chromones may assume under appropriate reaction conditions the *o*-quinodimethane structure. So the chromones belonging to the above named three categories may undergo Diels-Alder reaction with various dienophiles to give tetrahydroxanthone derivatives. Formation of xanthones via an initial [2+2]cycloaddition of alkynic dienophiles with 2- or 3-ethenylchromone is also feasible.

2-Ethenylchromones as the 4π components : The wrong structure **17** previously assigned without any spectroscopic data[10] to the cycloadduct obtained from *E*-2-styrylchromone **16** (R^1 = R^3 = H, R^2 = Ph) and maleic anhydride or *N*-phenylmaleimide (NPMI) has been rectified as the 1,2,3,4-tetrahydroxanthone **18** (R^1 = H, X = O or NPh)[11]. The cycloaddition of *E*-2-(1-methylstyryl)chromone **16** (R^1 = Me, R^2 = Ph, R^3 = H) with the aforesaid dienophiles also gives the xanthones **18** (R^1 = Me, X = O, NPh)[11]. Here the Diels-Alder (*endo*-addition) reactions are clearly followed by 1,3-hydrogen shift from C-9a to C-4 and presumably the driving force for this shift is the formation of the resonance stabilised chromone system. In the light of this report[11], the reported structures of the cycloaddducts of maleic anhydride or NPMI[12], dibenzoylethenes[13], and 1,4-benzo-quinones[14] with 2-styrylchromones may also need revision.

The reaction between 2-vinylchromones **16** (R^1 = Me, Ph, R^2 = Ph, R^3 = H; $R^1 = R^3$ = H, R^2 = Me, 2-furfuryl) and 1-pyrrolidinylcyclopentene **19** (*n* = 1) gives the xanthone derivatives **20**; the stereochemistry of the products indicates that the initial step in the reaction is an *exo*-addition Diels-Alder reaction with the inverse electron demand leading to the *cis*-fused C/D ring intermediate that rearranges to the chromone system and eliminates pyrrolidine molecule[5]. The aforesaid cyclopentene gives with **16** (R^1 = H, R^2 = Ph, R^3 = Me) a Michael adduct instead of any cycloadduct[15]. It is relevant to mention here that though the pentenedione **21**



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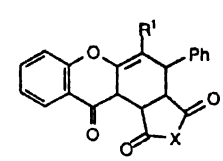

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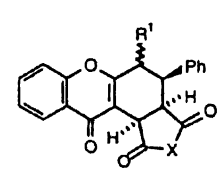

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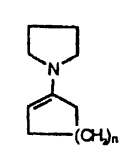

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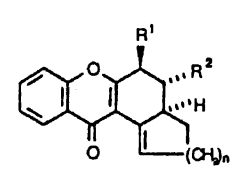

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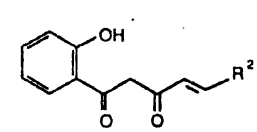

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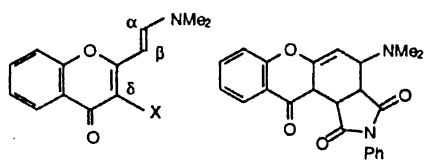
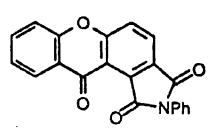
(R^2 = Ph or 2-furfuryl) also gives with the enamine **19** (*n* = 1 or 2) in boiling ethanol the cycloalkano[*a*]xanthone **20** (R^1 = H), this reaction does not involve conversion of **21** to the diene system **16** (R^1 = R^3 = H, R^2 = Ph or 2-furfuryl) followed by cycloaddition, hydrogen shift and elimination as described above[16].

The 2-vinylchromone **22**, because of the strong electron-releasing dimethylamino group, seems to be a more electron-rich diene than the analogous 2-styrylchromone **16** (R^1 = R^3 = H, R^2 = Ph) and the reactions of **22** and the corresponding 3-acyl derivatives **23** and **24** with various dienophiles have been studied in the present laboratory[17,18]. None of the dienes **22-24** react with NPMI in refluxing tolu-



22 X = H
23 X = Ac
24 X = COPh

25



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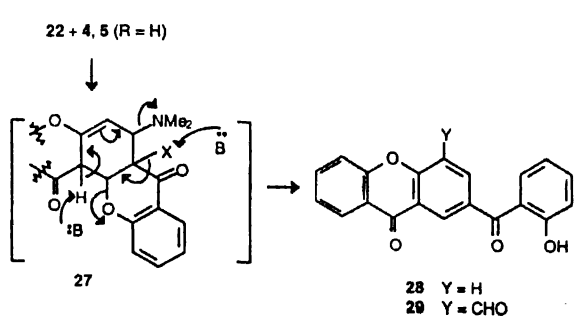
ene. The dienamine **22** with NPMI in refluxing dimethylformamide (DMF) produces the xanthone **26** evidently through the [4+2]cycloadduct **25** that readily eliminates dimethylamine and is dehydrogenated under reaction conditions. NPMI can also dehydrogenate **25** or the corresponding dehydroaminated compound and itself is reduced to *N*-phenylsuccinimide. The diene **22** in refluxing DMF gives **28** exclusively with acid **5** (R = H) but a mixture of **28** and **29** with the aldehyde **4**. Here the 3-substituted chromone **5** (R = H) (or **4**) forms with **22** the [4+2]cycloadduct **27** (X = CO_2H or CHO) which trasforms into **28** by base catalysed dehydrodimethylamination and decarboxylative (or deformylative) pyran ring opening, the adduct **27** itself functioning as the base (Scheme 1). The xanthone **29** results from an initial Michael addition of **22** to the chromone **4**[18].

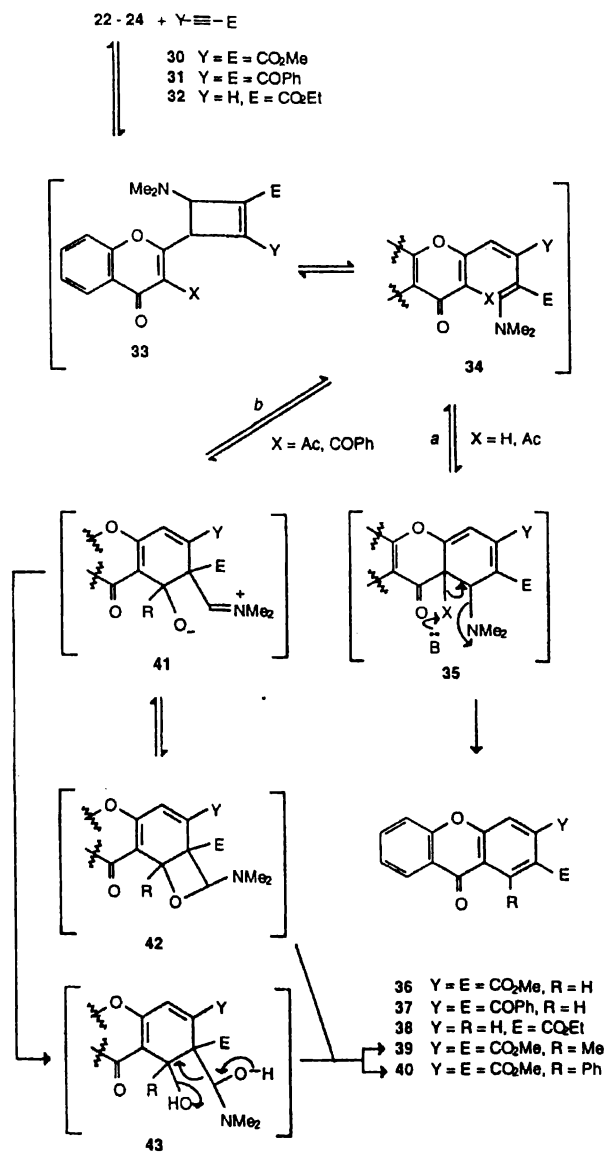
The dienamine **22** with dimethyl acetylenedicarboxylate (DMAD) **30** and dibenzoylacetylene **31** in refluxing DMF gives exclusively the xanthones **36** and **37**, respectively[17,18]. Here **22** behaves like an unconjugated enamine in undergoing [2+2]cycloaddition with the acetylenes **30** and **31** to give the adduct **33** (X = H) which isomerises to **34** (Scheme 2); the ring opened intermediate **34** incorporating a pre-existing double bond at the pyran 2,3-position behaves as a hexatriene system which by electrocyclisation (→ **35**) and



27

28 Y = H
29 Y = CHO

Scheme 1



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42

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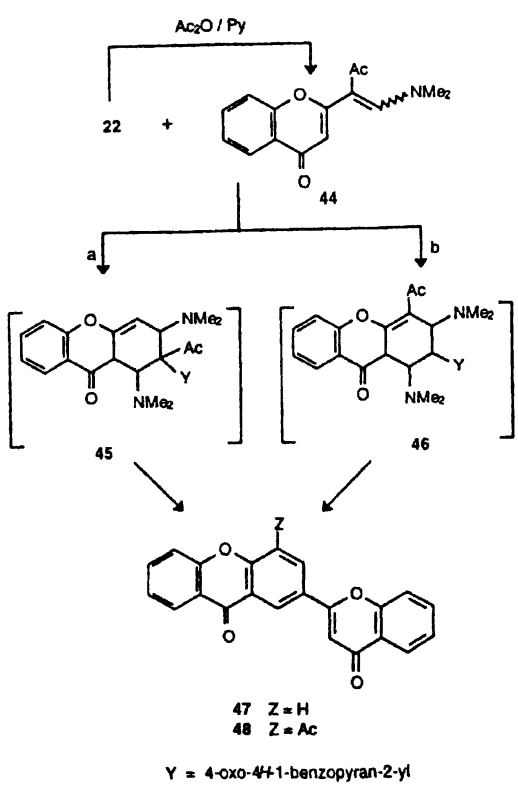
Scheme 2

subsequent elimination of dimethylamine gives the xanthones **36** and **37** (Scheme 2, path *a*). Ethyl propiolate **32** similarly gives with **22** the xanthone **38** admixed with 3′,5′-bis(ethoxycarbonyl)flavone.

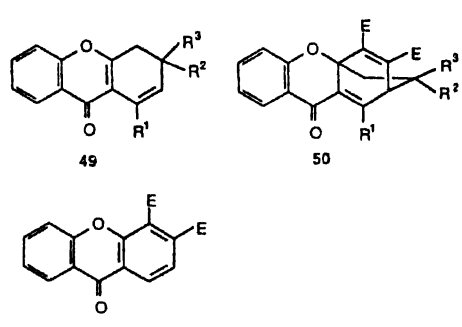
The enaminone **23** gives with DMAD the xanthones **36** and **39** admixed with 1-hydroxyxanthone (*vide infra*)[18]. The formation of the former two products indicates that the acetyl group at 3-position of **23** does not prevent its initial [2+2]cycloaddition with **30** to **33** (X = Ac) and the 1,9*a*-didhydroxanthone intermediate **35** obtained therefrom undergoes base catalysed deacylative deamination to **36** (Scheme 2, path *a*). The formation of **39** has been rationalised as follows : the enamine intermediate **34** (X = Ac) by intramolecular addition [→ **41** (R = Me)] and subsequent cyclisation gives the fused oxetane **42** that undergoes thermal cycloreversion to **39** and DMF (Scheme 3, path *b*). An alternative pathway for the formation of **39** involving addition of water to the zwitterion **41** (R = Me) and subsequent elimination of DMF and water from the resultant intermediate **43** may not be ruled out, formation of the resonance stabilised xanthone system being the driving force for the envisaged elimination process. The dienaminone **24** with DMAD **30** gives exclusively the xanthone **40** by the mechanism as depicted in Scheme 2, path *b*.



Scheme 3

Treatment of the dienaminone **22** with acetic anhydride-pyridine gives a mixture of the xanthones **47** and **48**[19]. The formation of both these products proceeds through initial β-acetylation of **22** to **44**, the latter functioning as a dienophile as well as an electron-deficient diene to undergo [4+2]cycloddition with the former. Thus, in the normal Diels-Alder reaction between the diene **22** and the dienophilic $Me_2NCH{=}CCOMe$ moiety of **44** gives the adduct **45** which by base catalysed dehydroamination and deacylative deamination affords **47** (Scheme 3, path *a*). The umpolung Diels-Alder reaction between the electron-deficient diene **44** with the electron-rich enamine moiety of **22** forms the cycloadduct **46** that affords **48** by elimination of two molecules of dimethylamine (Scheme 3, path *b*).

3-Ethenylchromones as the 4π components : Simple 3-ethenylchromones, because of their non-accessibility, have not yet been subjected to Diels-Alder reaction. 3,4-Dihydroxanthone **49** (R^1, R^2, R^3 = H, Me) having its diene portion locked in the *cis*-configuration undergoes facile D-A reaction with various diienophiles[20]. DMAD reacts with **49** (R^1-R^3 = H) as well as **49** (R^1 = H, R^2 = R^3 = Me) in boiling bromobenzene to give the same xanthene-dicarboxylic ester **51** as a result of an initial [4+2]cycloaddition (→ **50**) and a subsequent retro-Diels-Alder elimination of the alkyl bridge in the form of ethene and isobutene, respectively[20].



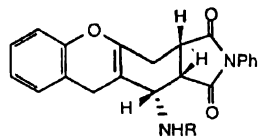
2,3-Disubstituted chromones as the 4π components : The *N,N*-dimethylhydrazone **52** and the anil **53** of 2-methyl-4-oxo-4*H*-1-benzopyran-3-carbaldehyde participate through the corresponding enehydrazine and enamine tautomers **54** D-A reaction with NPMI giving the adducts **55** (R = NMe_2 and C_6H_4Me-*p*) convertible by palladised charcoal into the xanthone derivatives **56** and **57**, respectively[21].

Annulation involving a Michael Initiated Ring Closure (MIRC) reaction :

3-Acetylchrome **58** (R^3 = H, R^4 = Me) dissolved in etha-

52 R = NMe_2
53 R = C_6H_4Me-*p*

54



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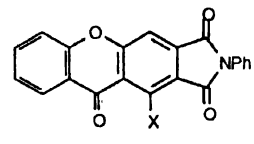
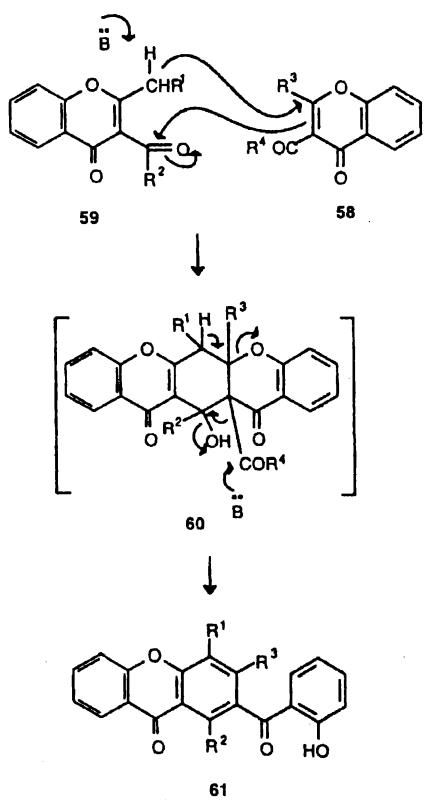


56 X = H
57 X = NHC_6H_4Me-*p*

nol or dioxane on treatment with pyridine or triethylamine or Brockman 'neutral' alumina affords the xanthone **61** (R^1-R^3 = H). This reaction was previously rationalised by base (or alumina) catalysed acyl-acyl rearrangement of 3-acetylchromone to 3-formyl-2-methylchromone **59** (R^1 = R^2 = H), [4+2]cycloaddition of the latter through its enol tautomer **54** (OH in place of NHR) with the former and base catalysed elimination and deacetylative elimination reaction of the resultant cycloadduct **60** (R^1-R^3 = H, R^4 = Me)[22]. Later on, the above mentioned self-condensation of 3-acetylchromone and that of 3-formyl-3-methylchromone



59 58

60

61

Scheme 4

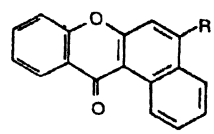
59 (R^1 = R^2 = H) to **61** (R^1 = R^2 = H, R^3 = Me) in refluxing pyridine-piperidine and of 3-acetyl-2-methylchromone **59** (R^1 = H, R^2 = Me) to **61** (R^1 = H, R^2 = R^3 = Me) in the presence of molecularised sodium indicate that 3-acyl-2-methylchromone **59** (R^1 = H, R^2 = H, Me) undergoes base catalysed MIRC reaction with the appropriate 3-acylchromone **58** to give the intermediate **60** which by elimination and pyran ring opening results in the 2-salicyloylxanthone **61** (Scheme 4)[23]. Unlike pyridine-piperidine catalysed self-condensation of 3-formyl-2-methylchromone to xanthone **61** (R^1 = R^2 = H, R^3 = Me), alumina converts the above named chromone to **61** (R^1-R^3 = H)[24] presumably by isomerisation of 3-formyl-2-methylchromone to 3-acetylchromone followed by a MIRC reaction between the two with subsequent elimination as shown in Scheme 4. Treatment of 3-formylchromone with phenyldiazomethane gives the xanthone **61** (R^1 = Ph, R^2 = R^3 = H)[25]. Here phenyldiazomethane brings about *C*-benzylation of 3-formylchromone to **59** (R^1 = Ph, R^2 = H) that reacts with the substrate **58** (R^3 = R^4 = H) to give the above named xanthone through the intermediate **60** (R^1 = Ph, R^2-R^4 = H), diazoalkane itself functioning as the base to catalyse the envisaged elimination process (Scheme 4).

Incorporation of one carbon component

Synthesis of xanthone by incorporation of one carbon component into the chromone system is illustrated by the Vilsmeier reaction of 3-acetyl-2-methylchromone with DMF-$POCl_3$ leading to 1-chloro-2-formyl-9*H*-xanthen-9-one[23]. Here the formylating agent brings about bisformylation of the ketomethyl of the substrate **58** (R^3 = R^4 = Me) followed by cyclisation and substitution of the hydroxy group by chlorine.

[6+0]Cyclisation of the appropriate 2- or 3-substituted and 2,3-disubstituted chromones

2-Styrylchromone **16** (R^1 = R^3 = H, R^2 = Ph) and 2-styrylisoflavone **16** (R^1 = H, R^2 = Ar, R^3 = Ph) in benzene on irradiation in the presence of iodine give the unsubstituted benzo[*a*]xanthone **62** (R = H)[26] and the corresponding 5-aryl analogue **62** (R = Ar)[27], respectively. The cycloadduct **63** of 3-formylchromone and ethyl vinyl ether[28] on treatment with acetone under acidic conditions gives the diketone **7**; the corresponding oxime **8** on heating under reflux in nitrobenzene undergoes electrocyclisation and subsequent oxidation to the oxime of 3-acetylxanthone[29]. Irradiation of 2-methyl-3-(2-methylbenzoyl)chromone **64** gives benzo[*b*]xanthone **65** (XY = ZR^1 = bond, R^2 = Me) by photoenolisation, 1,7-sigmatropic shift, electrocyclisation and oxida-



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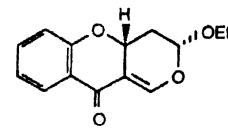

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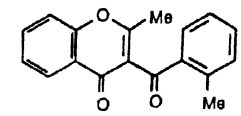

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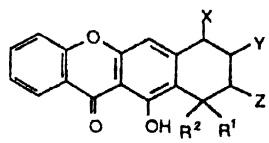

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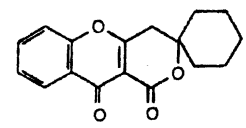

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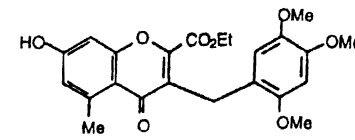

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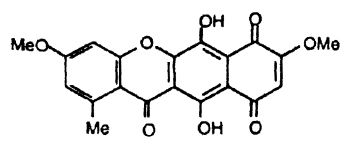

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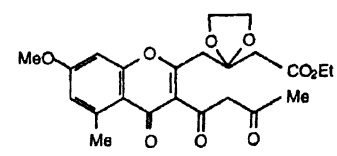

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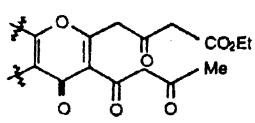

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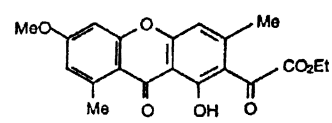

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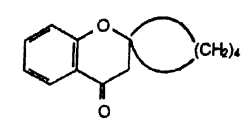

72

tion sequence[30]. Trifluoromethane sulphonic acid converts the lactone **66**, obtained by treating 3-carboxymethyl-2-methylchromone **58** (R^3 = Me, R^4 = OMe) with cyclohexanone in *t*-butanol and dimethoxyethane in the presence of potassium *t*-butoxide, into the cyclohexano[*b*]xanthone **65** (X-Z = R^1 = R^2 = H)[31]. The chromone derivative **67**, obtainable from 3,5-dihydroxytoluene, β-(2,4,5-trimethoxyphenyl)propionitrile and diethyl oxalate, has been converted in six steps into bikaverin **68**[32]. 3-Acetyl-2-(2-dimethylaminovinyl)chromone **23** on refluxing in DMF is converted through electrocyclisation of its enol form followed by elimination of dimethylamine into 1-hydroxyxanthone[18] whereas it gives 1-chloro-4-formylxanthone on treatment with DMF-$POCl_3$[23]. Preparation of **71** by cyclisation of the diketobenzopyran ester **69** involves a Wessely-Moser rearrangement of the triketone intermediate **70**[33]. It will not be out of context to mention here the formation of 1,2,3,4-tetrahydroxanthone by treating 2-spiro(cyclopentane)-chromanone **72** with thallium(III) nitrate in the absence or presence of an acid catalyst like boron trifluoride etherate, *p*-toluene sulphonic acid or perchloric acid[34].

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