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REACTIONS OF DIMETHYL ACETYLENEDICARBOXYLATE—X

REACTION WITH SALICYLALDEHYDE, ORTHO HYDROXYACETOPHENONE, 2-HYDROXYCHALCONES AND 2,2'-DIHYDROXYCHALCONES

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Abstract—Salicylaldehyde reacts with dimethyl acetylenedicarboxylate in benzene solution to give a mixture of dimethyl o-formylphenoxymaleate, dimethyl o-formylphenoxyfumarate, 2,3-dicarbomethoxychrom - 2 - en - 4 - ol, 2,3 - dicarbomethoxychrom - 3 - en - 2 - ol, dimethyl (2,3 - dicarbomethoxychrom - 2 - en - 4 - yl) - oxalacetate and dimethyl fumarate. 2,3 - Dicarbomethoxychrom - 3 - en - 2 - ol in this reaction is formed from 2,3 - dicarbomethoxychrom - 2 - en - 4 - ol through a benzopyrylium intermediate. The reaction of salicylaldehyde with excess of dimethyl acetylenedicarboxylate, however, gives a mixture of 2,3 - dicarbomethoxychrom - 3 - en - 2 - ol and dimethyl (2,3 - dicarbomethoxychrom - 3 - en) - 2 - oxyfumarate. 2,3 - Dicarbomethoxychrom - 3 - en - 2 - ol itself reacts further with dimethyl acetylenedicarboxylate to give 2,3,12 - tricarbomethoxychrom - 3,4 - eno[2,3 - b] pyrone. Similarly, the reaction of o-hydroxyacetophenone with dimethyl acetylendicarboxylate gives a mixture of dimethyl o-acetylphenoxymaleate, dimethyl o-acetylphenoxyfumarate, 2,3 - dicarbomethoxy - 4 - methylchrom - 2 - en - 4 - ol and 2,3 - dicarbomethoxy - 4 - methylchrom - 3 - en - 2 - ol. Both 2-hydroxychalcone and 2 - hydroxy - 4' - methoxychalcone give mixtures of chalcone - 2 - oxymaleate and chalcone - 2 - oxyfumarate. The reaction of 2,2'-dihydroxychalcone, however, gives 2'-hydroxyflavone, in addition to the expected maleate and fumarate. Similar reactions of 5 - chloro - 2,2' - dihydroxychalcone and of 3,5 - dibromo - 2,2' - dihydroxychalcone, on the other hand, give 2,3 - dicarbomethoxy - 4 - (o - hydroxyphenacyl) - 6 - chlorochrom - 2 - ene and 2,3 - dicarbomethoxy - 4 - (o - hydroxyphenacyl) 6,8 - dibromochrom - 2 - ene, respectively, together with the corresponding maleates and fumarates.

In general, phenols react with acetylenic esters to give a mixture of phenoxymaleates and phenoxyfumarates,[1] arising through a cis- or trans-mode of addition. Heindel and Schaeffer[2] have shown that the reaction of phenols containing suitably positioned functional groups such as salicylamides and salicylanilides with dimethyl acetylenedicarboxylate give a mixture of 1:1-adducts which can be converted to 1,3 - benzoxazin - 4 - ones, on treatment with a base. A similar reaction of methyl salicylate with dimethyl acetylendicarboxylate has been reported to give a mixture of dimethyl o-carbomethoxyphenoxymaleate and dimethyl o-carbomethoxyphenoxyfumarate.[2]

The object of the present investigation was to examine the reactions of a few o-hydroxy aldehydes, ketones and related nucleophiles with dimethyl acetylenedicarboxylate for the synthesis of heterocyclic systems. In this connection we have studied the reactions of salicylaldehyde, o-hydroxyacetophenone, 2-hydroxychalcones and 2,2'-dihydroxychalcones. Treatment of an equimolar mixture of salicylaldehyde **1a** with dimethyl acetylenedicarboxylate in benzene at 30° for 30 hr gave a 24% yield of a mixture of dimethyl o-formylphenoxyfumarate **4a** and dimethyl o-formylphenoxymaleate **5a**, consisting of 75% of **4a** and 25% of **5a** (by NMR). In addition, several other products were isolated which included 2,3 - dicarbomethoxychrom - 2 - en - 4 - ol **7a** (22%), 2,3 - dicarbomethoxychrom - 3 - en - 2 - ol **8a** (1%), dimethyl (2,3 - dicarbomethoxychrom - 2 - en - 4 - yl) - oxalacetate **13a** (1%) and dimethyl fumarate (0·5%) (Scheme 1). When the isomeric mixture consisting of dimethyl o-formylphenoxyfumarate **4a** and dimethyl o-formylphenoxymaleate **5a** was repeatedly chromatographed over silica gel it was possible to isolate a pure sample of **4a**, m.p. 84°. Attempts at isolating a pure sample of **5a** were not successful. The identity of **4a** was established on the basis of analytical and spectral data. The IR spectrum of **4a** showed two ester carbonyls at 1733 and 1725 cm^{-1}, whereas the absorption band at 1693 cm^{-1} was assigned to an aldehydic carbonyl group. The NMR spectrum of **4a** showed a singlet at 10·63 δ (1H), assigned to the aldehydic proton, a multiplet at 7·63 δ (4H) due to the aromatic protons and two singlets at 3·85 δ (3H) and 3·78 δ (3H), assigned to the two sets of ester methyl protons. The vinylic proton appeared as a sharp singlet at 6·87 δ (1H), which compares favourably with the chemical shifts of the vinylic protons in dimethyl o-carboxamidophenoxyfumarate (6·75 δ) and dimethyl o-carbomethoxyphenoxyfumarate (6·68 δ).[2] The presence of an aldehyde group in **4a** was confirmed through its 2,4-dinitrophenylhydrazone derivative, m.p. 241°.

The NMR spectrum of the mixture containing **4a** and **5a** showed the presence of two vinylic proton singlets at 6·87 δ and 5·40 δ. Of these, the signal at 6·87 δ was assigned to the vinylic proton in **4a**, and the one at 5·40 δ to the maleate isomer, **5a**. The vinylic proton position for **5a** at 5·40 δ compares favourably with the reported values for the proton positions in dimethyl o-carbomethoxyphenoxymaleates.[2]

The structure of **7a** has been deduced as 2,3 - dicarbomethoxychrom - 2 - en - 4 - ol, on the basis of analytical and spectral data. The IR spectrum of **7a** showed an OH absorption at 3465 cm^{-1} and ester carbonyl bands at 1722 and 1700 cm^{-1}, in addition to other characteristic spectral features of 2-chromenes.[3] The NMR spectrum of **7a** showed a multiplet centred at 7·47 δ (4H), assigned to the aromatic protons. The two ester methyl protons appeared as sharp singlets at 3·99 δ (3H)

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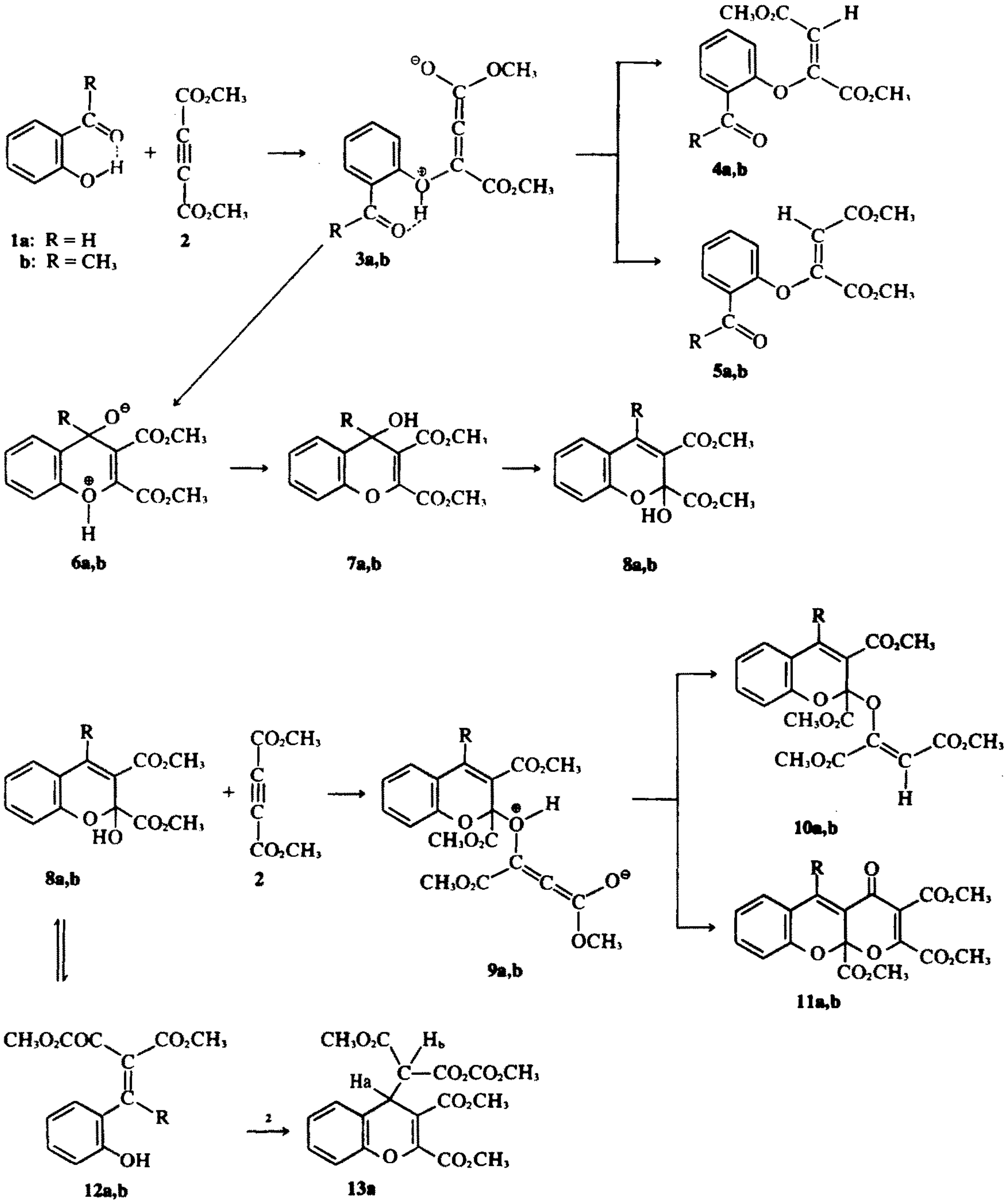


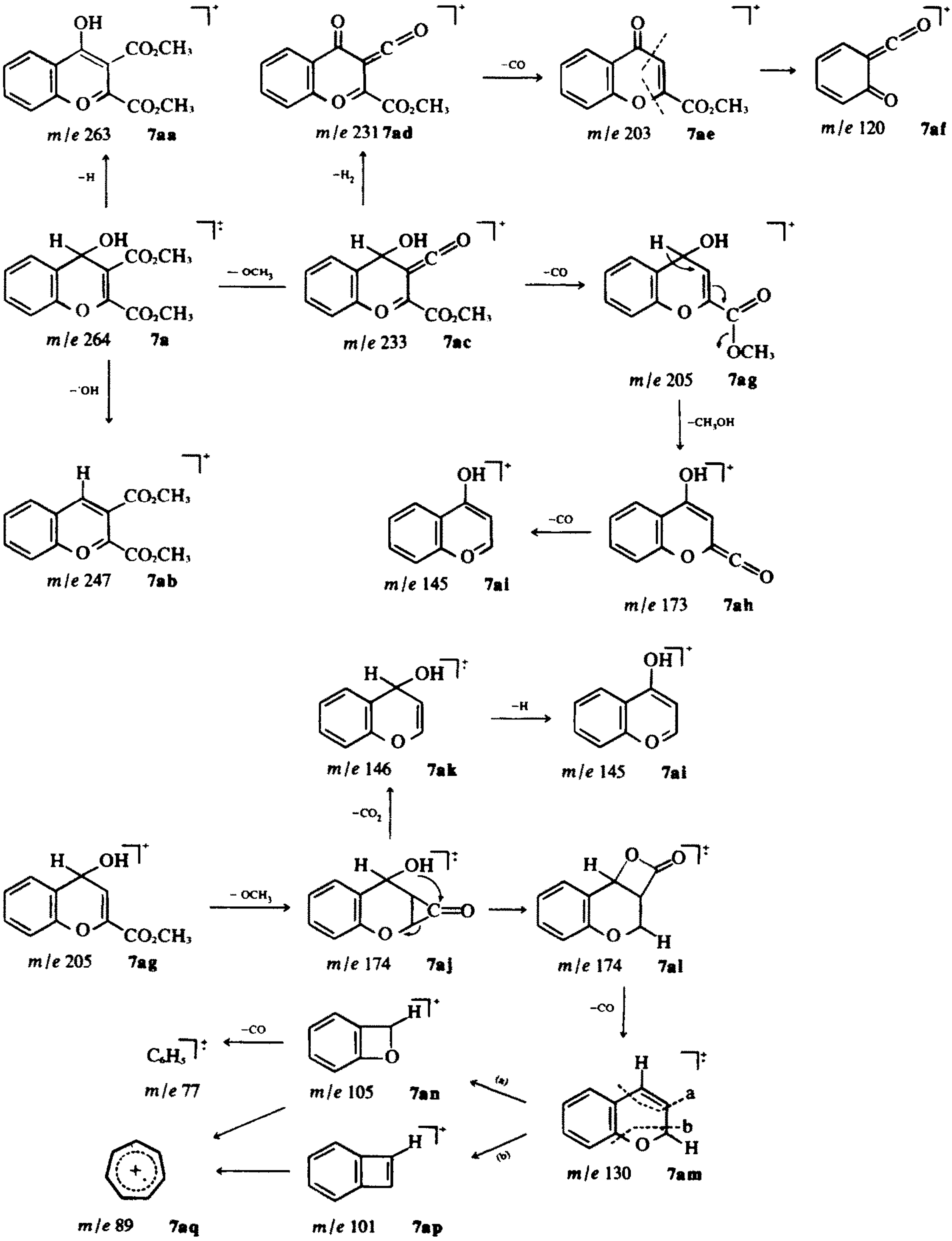
Scheme 1.

and 3·89 δ (3H). In addition, the spectrum showed a doublet at 5·83 δ (1H, J = 5·5 Hz), assigned to the C-4 proton and a second doublet at 3·29 δ (1H, J = 5·5 Hz), assigned to the C-4 hydroxyl proton. The NMR spectrum of **7a**, after D_2O exchange showed a singlet at 5·83 δ, due to the C-4 proton, whereas the signal at 3·29 δ due to the hydroxyl proton completely disappeared, as expected.

Further support for the chromenol structure of **7a** was derived from its UV spectral data. The UV spectrum of **7a** in methanol showed a single absorption maximum at 264 nm (ε, 6,300), whereas the spectrum in 98% sulphuric acid was characterised by the presence of two absorption maxima at 265 nm (ε, 24,900) and 348 (13,400).[3c] The appearance of two absorption maxima in a strong sulphuric acid solution of **7a** indicated the formation of the benzopyrylium ion intermediate, **14a**. The NMR spectrum of **7a** in 98% sulphuric acid solution also supported this assumption. Thus, the NMR spectrum showed a multiplet around 8·73 δ (5H), assigned to the aromatic protons, whereas the two sharp singlets at 4·52 δ (3H) and 4·43 δ (3H) were assigned to the ester methyl protons at the C-2 and C-3 positions, respectively, which are comparable with the ester methyl protons of methyl acetate, for example, which appear at 4·53 δ.[4]

Additional support for the structure **7a** was derived from electron impact studies. The mass spectrum of **7a** showed the molecular ion peak at *m/e* 264 (47%). Other prominent peaks were observed at *m/e* 263 (93%), 247

(90%), 233 (58%), 231 (93%), 219 (35%), 205 (100%), 203 (40%), 174 (22%), 173 (81%), 146 (54%), 145 (38%), 130 (31%), 120 (26%), 105 (55%), 101 (54%), 89 (47%) and 77 (50%), most of which could be assigned to the fragments shown in Scheme 2. Loss of a proton from the molecular ion, **7a**, would result in the formation of the stable benzopyrylium cation **7a**, with *m/e* 263. Alternatively, the molecular ion may lose the hydroxyl radical to give the benzopyrylium cation **7ab**, *m/e* 247. The fragment at *m/e* 233 could be due to **7ac**, formed by the loss of a methoxyl group from the molecular ion. Further loss of two protons could result in the formation of **7ad**, with *m/e* 231, which may lose CO to give the fragment **7ae**, at *m/e* 203. The peak at *m/e* 120 may arise from the fragment **7af** formed by fission of both the bonds β to the benzene ring of **7ae**, as has been reported in the case of other γ-pyrones.[5] Alternatively, **7ac** may lose CO to give **7ag**, with *m/e* 205, which was the base peak in the mass spectrum. The peak



Scheme 2.

at m/e 173 could be assigned to **7ah** formed by the loss of the elements of methanol from the cation **7ag**. The fragment **7ah** may further lose CO to give the cation **7ai**, with m/e 145. Alternatively, **7ag** may lose a methoxyl radical to give the fragment **7aj**, m/e 174. The peak at m/e 146 may be due to **7ak** formed by the loss of a carbomethoxy group from **7ag**, which may in turn lose a proton to give the benzopyrylium cation **7al**, m/e 145. The fragment **7aj**, at m/e 174 may rearrange to **7al**, m/e 174, followed by the loss of CO_2 to give **7am**, with m/e 130. The peaks at m/e 105 and 101 may be due to the fragments **7an** and **7ap**, respectively. Both these fragments may give rise to **7aq**, with m/e 89. Loss of CO from **7an** may lead to the phenyl cation, with m/e 89. Loss of CO from **7an** may lead to the phenyl cation, with m/e 77.

To confirm the structure of **7a**, we attempted its oxidation to a chromone derivative. Treatment of **7a** with excess of nickel peroxide in refluxing benzene gave a 61% yield of dimethyl chromone - 2,3 - dicarboxylate **16**. The IR spectrum of **16** showed two ester carbonyls at 1742 and 1732 cm^{-1}, whereas the keto carbonyl and the olefinic absorptions were observed at 1648 and 1631 cm^{-1}, respectively. The UV spectrum of **16** in methanol showed absorption maxima at 236 nm (ϵ, 13,600), 250 (sh, 8,400), 258 (sh, 6,300), 314 (6,200) and an absorption minimum at 279 (2,900), characteristic of chromone derivatives.[6]

Further confirmation of the chromone structure for **16** was derived from its NMR spectrum. The aromatic protons in **16** appeared as a multiplet centred around 7·68 δ (3H) and a pair of poorly resolved doublets centred around 8·38 δ (1H) (J = 8·5 Hz and 1·2 Hz). The multiplet around 7·68 δ is assigned to the protons at C-6, C-7 and C-8 positions, whereas the pair of doublets around 8·38 δ may be assigned to the C-5 proton resonance, which is split by both the C-6 and C-7 protons ($J_{5,6} = 8{\cdot}5$ Hz and $J_{5,7} = 1{\cdot}2$ Hz). The C-5 proton in chromones generally appears around 8·2 δ ($J_{5,6} = 8{\cdot}5$ Hz; $J_{5,7} = 1\text{–}1{\cdot}25$ Hz);[7] the downfield shift for the C-5 proton may be ascribed to the deshielding effect of the carbonyl function at C-4. The spectrum of **16** showed, in addition, two singlets at 4·10 δ (3H) and 4·05 δ (3H) assigned to the two sets of ester methyl protons.

Analytical results and spectral data show that the adduct **8a** is best represented as the cyclic 2,3 - dicarbomethoxychrom - 3 - en - 2 - ol and not the open chain phenolic ketone, **12a** (Scheme 1). The IR spectrum of this adduct showed an OH absorption band at 3460 cm^{-1}, two ester carbonyl absorptions at 1731 and 1704 cm^{-1} and other characteristic absorption bands of 3-chromenes.[3b] However, the spectrum did not show the presence of any band due to an α,β-unsaturated carbonyl function, which would be expected if the adduct has structure **12a**. The NMR spectrum of the adduct showed a singlet at 7·98 δ (1H) due to the olefinic proton at C-4 and a multiplet centred around 7·40 δ (4H), due to the aromatic protons. The two sets of ester methyl protons appeared as sharp singlets at 3·96 δ (3H) and 3·89 δ (3H). In addition, the spectrum showed the presence of an exchangeable proton singlet at 5·27 δ (1H), due to the hydroxyl group.

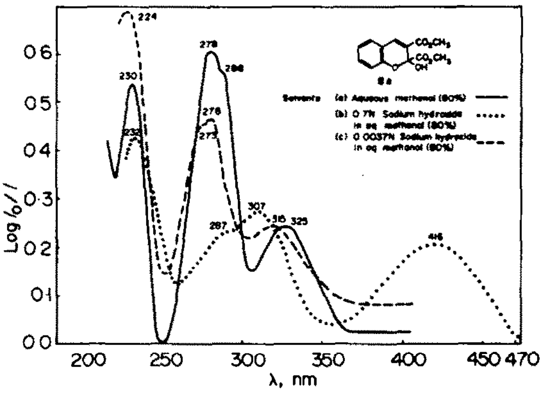
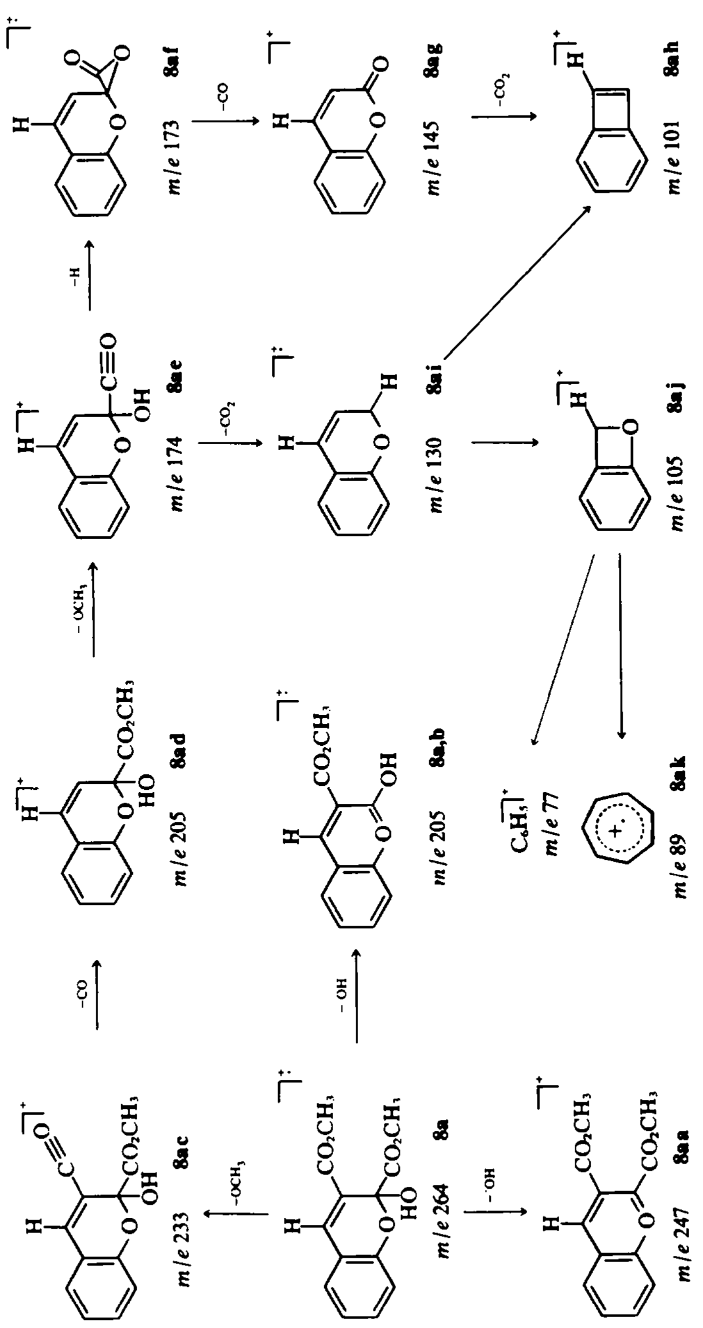


Fig. 1. UV spectrum of 2,3 - dicarbomethoxychrom - 3 - en - 2 - ol **8a**.

Further evidence concerning the structure of **8a** was derived from UV spectral studies. The UV spectrum of the adduct in aqueous methanol (1 : 4) showed absorption maxima at 230 nm (ϵ, 16,600), 278 (17,500), 288 (sh, 12,700) and 325 (7,400) (Fig. 1a). There was practically no change in the spectrum when determined in aqueous methanol containing a small amount of sulphuric acid (2%). However, the spectrum of this adduct showed marked change in concentrated sulphuric acid (98%), and was identical with that of the benzopyrylium ion **14a**, generated from **7a**. The UV spectrum in methanolic sodium hydroxide solution (0·7 N), however, showed absorption maxima at 232 nm (ϵ, 12,600), 287 (sh, 8,000), 307 (9,800) and 416 (7,100) (Fig. 1b). The bathochromic shift of the different bands observed in alkaline medium suggests that the cyclic hemiacetal, **8a** is undergoing ring opening to the open chain phenolic ketone **12a**, which may be present as the phenoxide ion. However, in very dilute alkaline medium (0·0037 N), the spectrum showed absorption maxima at 224 nm (ϵ, 20,700), 273 (sh, 13,900), 276 (14,000) and 315 (7,700) (Fig. 1c). That this spectrum resembles the one in strongly alkaline medium (Fig. 1b), except for slight hyposchromic shifts of the bands, would suggest that Fig. 1c represents the spectrum of the open chain form of the adduct, **12a**. From these studies, it appears that both in neutral and slightly acidic media, **8a** exists in the hemiacetal form.

Additional support for the chromenol structure **8a** was derived from electron-impact studies. The mass spectrum of **8a** showed the molecular ion peak at m/e 264 (3%). Other prominent peaks in the mass spectrum were observed at m/e 247 (27%), 233 (9%), 206 (80%), 205 (100%), 174 (100%), 173 (100%), 146 (52%), 145 (69%), 130 (24%), 118 (52%), 105 (18%), 101 (79%), 90 (51%), 89 (78%), 77 (38%) and 75 (46%), most of which may be assigned to the fragments shown in Scheme 3. The loss of hydroxyl group from the molecular ion will give the stable benzopyrylium ion **8aa**, m/e 247. Alternatively, the molecular ion may lose the C-2 carbomethoxy group to give the more stable benzopyrylium cation **8ab**, m/e 205, which was the base peak in the spectrum. Such a low intensity of the molecular ion peak and the formation of the highly stable benzopyrylium cations are in agreement with the known electron impact behaviour of other 3-chromenes.[5b,8] The peak at m/e 233 may be due to the fragment **8ac** formed by the loss of a methoxy group from the molecular ion. Further loss of CO would lead to the fragment **8ad**, with m/e 205, which may in turn lose a methoxyl group to give **8ae**, with m/e 174 (100%). This may further lose a proton to give the cation **8af** with m/e 173. The peak at m/e 145 may be due to the fragment **8ag**, formed by the loss of CO from **8af**. This may in turn lose CO_2 to give **8ah**, with m/e 101. Alternatively, **8ae** may lose CO_2 to give **8ai**, m/e 130 which may in turn give **8aj**, at m/e 105 and **8ah**, at m/e 101. The peak at m/e 77 may be


m/e 264 8a
-OCH3
m/e 233 8ac
-CO
m/e 205 8ad
-OCH3
m/e 174 8ae
-H
m/e 173 8af
-CO
m/e 145 8ag
-CO2
m/e 101 8ah
-OH
m/e 205 8a,b
-CO2
m/e 130 8ai
m/e 105 8aj
-OH
m/e 247 8aa
C6H5
m/e 77
m/e 89 8ak

Scheme 3.

due to the phenyl cation formed by the loss of CO from **8aj**. Both the fragments **8ah** and **8aj** can give **8ak**, with *m/e* 89.

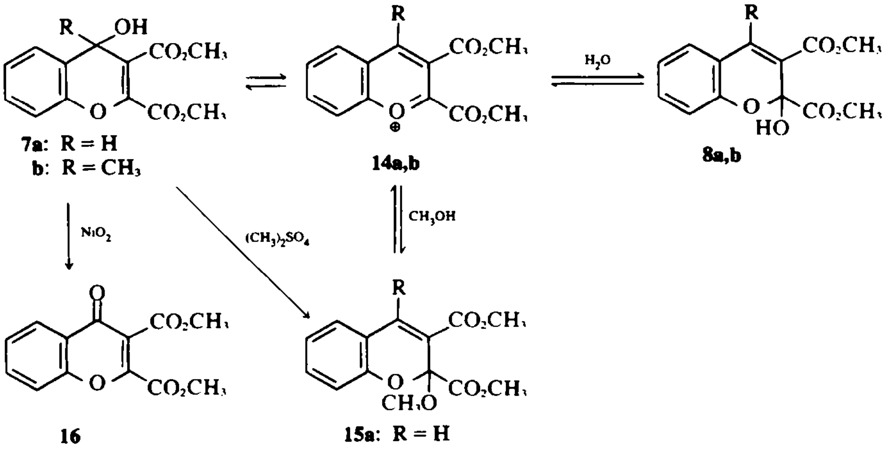
Analytical results show that the product **13a** should be represented by the formula $C_{19}H_{18}O_{10}$, a compound formed by the addition of two moles of dimethyl acetylenedicarboxylate to one of salicylaldehyde. The IR spectrum of **13a** showed two ester carbonyl absorptions at 1750 and 1734 cm^{-1} and a keto carbonyl at 1708 cm^{-1}, whereas it did not show the presence of any hydroxyl group. The NMR spectrum of **13a** showed a multiplet centred around 7·18 δ (4H), assigned to the aromatic protons and singlets at 4·03 δ (3H), 3·90 δ (3H), 3·86 δ (3H) and 3·63 δ (3H), assigned to the four sets of ester methyl protons. In addition, the spectrum showed two doublets at 4·60 δ (1H, J = 3·0 Hz) and 3·68 δ (1H, J = 3·0 Hz), assigned to the two tertiary protons labelled as H_a and H_b, respectively.

The reaction of a substituted phenol such as salicylaldehyde **1a** with dimethyl acetylenedicarboxylate would be expected to proceed through a resonance stabilized zwitterionic intermediate **3a** (Scheme 1). This intermediate can pick-up a proton either internally to give the cis-addition product, **5a**, which has the maleate geometry or externally to give the trans-addition product, **4a**, which has the fumarate geometry. Alternatively, the zwitterionic intermediate **3a** can give rise to the chromen - 4 - ol derivative **7a**, through the intermediate **6a**. One of the possible routes to the formation of **8a** is through the isomerization of **7a**, under acidic conditions, involving the benzopyrylium cation **14a** (Scheme 4). The UV spectrum of an aqueous methanolic (1:4) solution of **7a**, containing small amounts of sulphuric acid was identical with the spectrum of **8a** in methanol solution, which shows that **7a** is readily isomerized to **8a**, under acidic conditions. It was possible to isomerize **7a** to **8a** in about 80% yield, in aqueous methanol containing hydrochloric acid and in about 88% yield in presence of silica gel. No isomerization of **7a** to **8a** was observed under basic conditions e.g. refluxing in the presence of potassium carbonate in benzene. Therefore, it is probable that either salicylaldehyde or one of its transformation products in the presence of a base, may induce isomerization of **7a**, under the reaction conditions. It was shown that **7a** undergoes isomerization to **8a** to the extent of about 20%, when refluxed in benzene in the presence of a mixture of salicylaldehyde and potassium carbonate.

If isomerization of **7a** to **8a** occurs through the benzopyrylium cation **14a**, as shown in Scheme 4, then it would be reasonable to assume that other nucleophiles capable of reacting with **14a** should give substituted chromene derivatives. It is pertinent to observe that the UV spectrum of a methanolic solution of **7a** containing 2% sulphuric acid was similar to the spectrum of **8a** in methanol, indicating that the benzopyrylium ion **14a** that is formed from **7a** may be reacting with methanol to give a methoxy derivative. It was shown that refluxing **7a** in absolute methanol in the presence of a catalytic amount of p-toluenesulphonic acid, gave a 99% yield of 2,3 - dicarbomethoxy - 2 - methoxychrom - 3 - ene **15a**. The identity of **15a** was established on the basis of analytical results and spectral data. The IR spectrum of **15a** did not show the presence of any OH band. The NMR spectrum of **15a** showed a singlet at 8·02 δ (1H), assigned to the C-4 olefinic proton. In addition, the spectrum showed a multiplet centred around 7·40 δ (4H), due to the aromatic protons and two singlets at 3·92 δ (6H) and 3·52 δ (3H), due to the ester methyl protons and C-2 methoxyl protons, respectively. The NMR spectrum of **15a** in sulphuric acid, however, showed a singlet at 4·26 δ (3H), in addition to the signals due to the benzopyrylium cation, **14a**. This signal at 4·26 δ may be assigned to methanol, generated during the formation of **14a** from **15a**. Methanol has been reported to show a signal at 4·30 δ.[4] Treatment of chromenol **8a** in absolute methanol with a small amount of sulphuric acid gave a 68% yield of **15a**. The formation of **15a** in this case may also proceed through the benzopyrylium cation **14a** (Scheme 4). A similar methyl ether formation, under analogous conditions, has been reported in the case of 6 - hydroxy - 6 - methylchromeno[4,3 - b]chromen - 7 - one.[9] Direct methylation of **8a** employing diazomethane also gave the 2-methoxychromene, **15a** (Scheme 4). The formation of **15a** in the reaction of **8a** with diazomethane suggests that **8a** exists in the cyclic hemiacetal form under neutral conditions.

In an attempt to prepare the methyl ether of **7a**, we treated **7a** with diazomethane but were unable to isolate any of the methylated product. However, the methylation of **7a** using dimethyl sulphate gave the methyl ether **15a** in 29% yield. The formation of **15a** in this reaction suggests that **7a** is undergoing an initial isomerization to **8a** under the reaction conditions, which undergoes subsequent methylation.

The formation of the 1:2-adduct, **13a** in the reaction of



Scheme 4.

salicylaldehyde with dimethyl acetylenedicarboxylate may be explained in terms of the initial transformation of the 2-chromenol, **8a** to give the phenolic derivative **12a**, which subsequently reacts with dimethyl acetylenedicarboxylate as shown in Scheme 1.

With a view to studying the nature of the products formed under different conditions, the reaction of salicylaldehyde with dimethyl acetylenedicarboxylate has been investigated in greater detail. Thus, the reaction when carried out using a 1:1 ratio of the reactants, in acetone for 30 hr at room temperature (30°) gave a 10% yield of **7a** and 8% yield of **8a**. In addition, a 29% yield of a mixture of **4a** and **5a** was obtained which was isolated through their 2,4-dinitrophenylhydrazone derivatives. When the same reaction was carried out in refluxing benzene, a 34% yield of **4a** and 23% yield of **8a**, together with a liquid mixture (7%) containing **4a** and **5a** in the ratio 88:12 were obtained.

When the reaction of salicylaldehyde with dimethyl acetylenedicarboxylate was carried out using a 1:2 molar ratio of the reagents, the only products that could be isolated were a 7% yield of **8a** and 5% yield of a product identified as dimethyl (2,3 - dicarbomethoxychrom - 3 - en) - 2 - oxyfumarate **10a**. Analytical results show that **10a** should be represented by the formula $C_{19}H_{18}O_{10}$, a compound formed by the addition of one mole of salicylaldehyde to two moles of dimethyl acetylenedicarboxylate. The IR spectrum of **10a** showed three ester carbonyl bands at 1756, 1735 and 1705 cm^{-1}. The NMR spectrum of **10a** showed a singlet at 7·60 δ (1H) assigned to the C-4 olefinic proton, whereas the aromatic protons appeared as a multiplet centred around 7·18 δ (4H). The four ester methyl groups appeared as three singlets 3·98 δ (3H), 3·86 δ (3H) and 3·80 δ (6H). In addition, the spectrum showed a singlet at 6·08 δ, assigned to the vinylic proton in the fumarate side-chain.

Further confirmation of the structure of **10a** was derived from its UV spectrum. The UV spectrum of **10a** in methanol was found to be similar to that of **8a** suggesting that **10a** may be a derivative of the chrom - 3 - en - 2 - ol, **8a**. The UV spectrum of **10a** in 98% sulphuric acid, however, was found to be identical with that of **7a** in 98% sulphuric acid, showing that the benzopyrylium ion **14a** is formed on treatment of **10a** with concentrated sulphuric acid. This conclusion was also reached from NMR studies of the sulphuric acid solution of **10a**, which showed a multiplet centred around 8·73 δ (5H), assigned to the ring protons of **14a**. In addition, the spectrum showed a multiplet centred around 4·33 δ (14H), assigned to the two sets of ester methyl protons of **14a** and the protons of dimethyl oxalacetate moiety formed in acid medium. Diluting the sulphuric acid solution of **10a** with aqueous methanol (2:3) gave **8a**, as identified from its UV spectrum.

To ascertain whether the hydroxyl groups in the chromenols **7a** and **8a** undergo further reaction with dimethyl acetylenedicarboxylate these reactions were examined separately. It was observed that **7a** did not undergo any addition reaction with dimethyl acetylenedicarboxylate in the presence of potassium carbonate, whereas the reaction of **8a** under these conditions gave a 37% yield of a compound identified as 2,3,12 - tricarbomethoxychrom - 3,4 - eno [2,3 - b]pyrone **11a**. Analytical results indicated that **11a** should be represented by the formula $C_{18}H_{14}O_9$, a product formed by the loss of a methanol fragment from a 1:1-adduct. The IR spectrum of **11a** showed two ester carbonyl bands at 1757 and 1748 cm^{-1} and a keto carbonyl at 1668 cm^{-1}. The olefinic C=C absorptions were observed at 1626 and 1616 cm^{-1}. The NMR spectrum of **11a** showed a multiplet centred around 7·32 δ (4H), assigned to the aromatic ring protons. The C-6 proton appeared as a sharp singlet at 7·82 δ. In addition, the spectrum showed three singlets at 4·02 δ (3H), 3·92 δ (3H) and 3·86 δ (3H), assigned to the three sets of ester methyl protons.

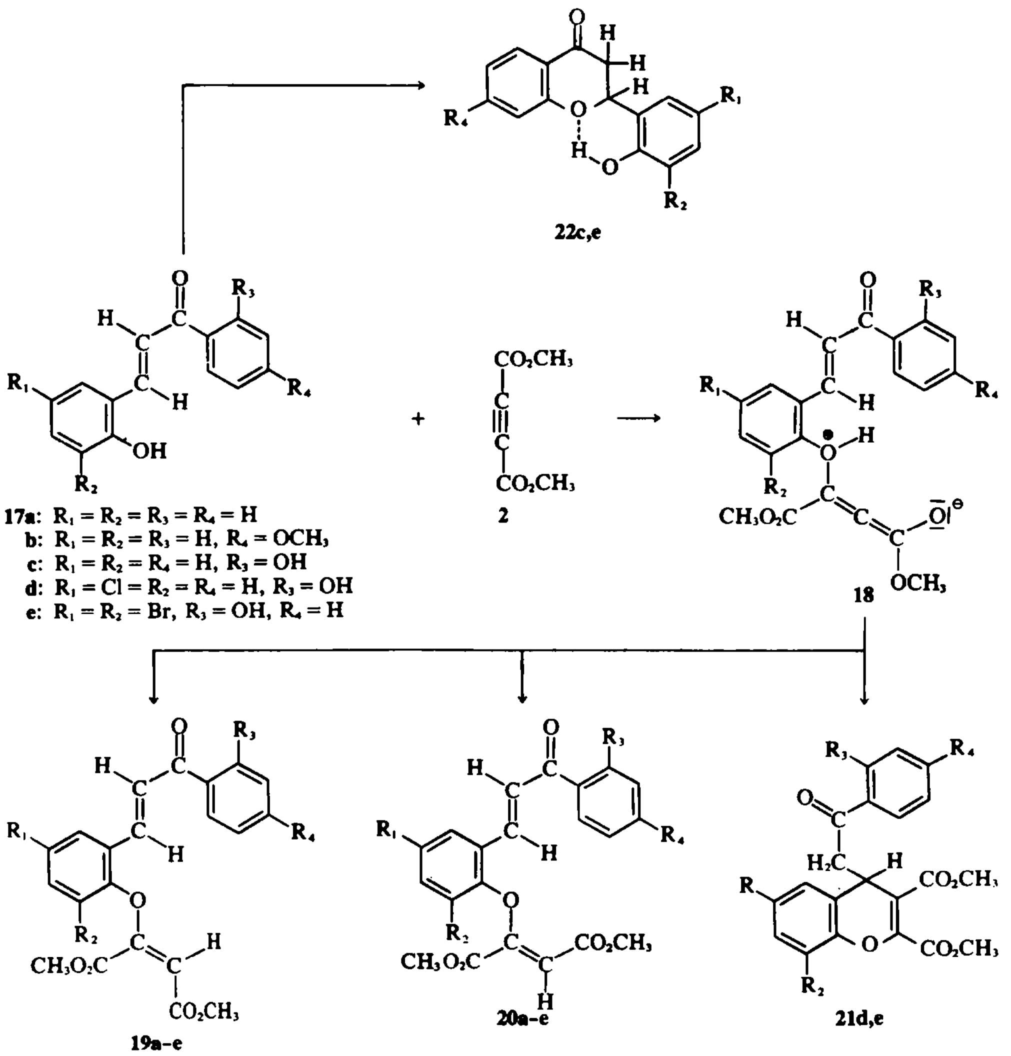
Similarly, the reaction of o-hydroxyacetophenone **1b** with dimethyl acetylenedicarboxylate in acetone around 30° gave a mixture of products consisting of 2,3 - dicarbomethoxy - 4 - methylchrom - 2 - en - 4 - ol **7b** (67%), 2,3 - dicarbomethoxy - 4 - methylchrom - 3 - en - 2 - ol **8b** (12%) and a 5% yield of a mixture of dimethyl o-acetylphenoxyfumarate **4b** and dimethyl o-acetylphenoxymaleate **5b**, consisting of 33% of **4b** and 67% of **5b** (by NMR). The identities of these products were established on the basis of analytical and spectral data. The UV spectrum of **7b** in methanol, for example, showed absorption maxima at 217 nm (ε, 17,800) and 267 (9,200).[3c] A spectrum of **7b** in 98% sulphuric acid, however, showed absorption maxima at 221 nm (ε, 15,500), 259 (22,800) and 347 (12,900), suggesting that the benzopyrylium ion **14b** is generated under acidic conditions.

A solution of **7b** in 98% sulphuric acid when diluted with aqueous methanol (1:4) shows a UV spectrum which is identical to that of the spectrum of the 2-chromenol, **8b**. This indicates that the benzopyrylium ion, **14b** is formed from **7b** in concentrated acid solution which is subsequently converted to **8b**, on dilution with aqueous methanol. In a separate experiment it was possible to isomerize **7b** to **8b**, in a 82% yield by adding water to a solution of **7b** in 98% sulphuric acid and in a 96% yield by shaking a solution of **7b** in chloroform with 1% hydrochloric acid. The isomerization of **7b** to **8b** has also been observed under thermal conditions. Thus refluxing a solution of **7b** in benzene for 48 hr gave a 40% yield of **8b**. Also, it has been observed that **7b** undergoes slow isomerization to **8b**, on keeping at room temperature for several months.

The reaction of o-hydroxyacetophenone with dimethyl acetylenedicarboxylate in refluxing acetone, however, gave a mixture of the 4-chromenol, **7b** (50%) and the 2-chromenol, **8b** (21%) as the only isolable products.

We have also examined the reactions of 2-hydroxychalcone, 2 - hydroxy - 4′ - methoxychalcone, 2,2′-dihydroxychalcone, 5 - chloro - 2,2′ - dihydroxychalcone and 3,5 - dibromo - 2,2′ - dihydroxychalcone with dimethyl acetylenedicarboxylate. Treatment of 2-hydroxychalcone **17a** with dimethyl acetylenedicarboxylate in refluxing benzene in presence of anhydrous potassium carbonate gave a mixture of dimethyl chalcone - 2 - oxymaleate **19a** (26%) and dimethyl chalcone - 2 - oxyfumarate **20a** (54%). The IR spectrum of **19a** showed two ester carbonyl bands at 1748 and 1716 cm^{-1}, and a keto carbonyl at 1685 cm^{-1}. The NMR spectrum of **19a** showed a multiplet centred around 7·76 δ (11H), assigned to the aromatic protons (9H) and two vinylic protons. The two sets of ester methyl protons appeared as sharp singlets at 3·75 δ (3H) and 4·02 δ (3H). In addition, the spectrum of **19a** showed a singlet at 5·27 δ (1H), assigned to the vinylic proton of the maleate side chain. The vinylic proton position at 5·27 δ compares favourably with the chemical shift of vinylic protons in analogous phenoxymaleates.[1a,2]

The IR spectrum of **20a** showed the presence of two



Scheme 5.

ester carbonyls at 1730 and 1713 cm^{-1} and a keto carbonyl absorption at 1658 cm^{-1}. The bands at 1648 and 1640 cm^{-1} were assigned to the olefinic absorptions. The NMR spectrum of **20a** showed a multiplet centred around 7·98 δ (11H) assigned to the aromatic protons (9H) and two vinylic protons. In addition, the spectrum showed a singlet at 6·82 δ (1H), assigned to the vinylic proton, of the fumarate side chain. The chemical shift of this proton compares favourably with the vinylic proton positions in other phenoxyfumarates reported.[1a,2] The two sets of ester methyl protons appeared as sharp singlets at 3·79 δ (3H) and 3·84 δ (3H). Attempts to cyclize **20a**, under acidic, basic and thermal conditions were unsuccessful.

An analogous reaction of 2 - hydroxy - 4′ - methoxychalcone **17b** with dimethyl acetylendicarboxylate gave a mixture of dimethyl 4′ - methoxychalcone - 2 - oxymaleate **19b** (23%) and dimethyl 4′ - methoxychalcone - 2 - oxyfumarate **20b** (60%).

Similarly, the reaction of 2,2′-dihydroxychalcone **17c** with dimethyl acetylenedicarboxylate gave a mixture of products consisting of dimethyl 2′ - hydroxychalcone - 2 - oxymaleate **19c** (27%), dimethyl 2′ - hydroxychalcone - 2 - oxyfumarate **20c** (51%) and 2′-hydroxyflavanone **22c** (9%). The structure of **22c** was deduced on the basis of analytical results, spectral data[10] and subsequent comparison with an authentic sample.[11] Thus, the UV spectrum of **22c**, for example, was found to be identical with the reported spectrum of 2′-hydroxyflavanone.[12]

The reaction of 5 - chloro - 2,2′ - dihydroxychalcone **17d** with dimethyl acetylenedicarboxylate under analogous conditions gave a 27% yield of dimethyl 5 - chloro - 2′ - hydroxychalcone - 2 - oxyfumarate **20d**, and 63% yield of a liquid mixture consisting of dimethyl 5 - chloro - 2′ - hydroxychalcone - 2 - oxymaleate **19d** (54%) and 2,3 - dicarbomethoxy - 4 - (o - hydroxyphenacyl) - 6 - chlorochrom - 2 - ene **21d** (46%), identified from its NMR spectrum. This showed a multiplet centred around 7·53 δ, assigned to the aromatic protons and two vinylic protons. The vinylic proton of the maleate side chain appeared as a sharp singlet at 5·23 δ, whereas the ester methyl protons appeared as four singlets at 3·72 δ, 3·80 δ, 3·95 δ and 3·99 δ. The hydroxyl proton appeared as an exchangeable singlet at 12·0 δ. This downfield chemical shift of the hydroxyl proton shows that it is strongly hydrogen bonded. In addition, the spectrum showed two poorly resolved multiplets around 4·55 δ and 3·43 δ, assigned to the C-4 proton and the methylene protons of the chromene, **21d**, respectively.

This mixture, consisting of **19d** and **21d** when repeatedly chromatographed over silica gel gave a pure sample of

21d. Analytical results showed that **21d** should be represented by the formula $C_{21}H_{17}ClO_7$. Its IR spectrum showed two ester carbonyl absorptions at 1750 and 1720 cm^{-1} and a keto carbonyl at 1640 cm^{-1}. In addition, the spectrum showed spectral features characteristic of 2-chromenes.[3] The NMR spectrum of **21d** showed the aromatic protons as a multiplet centred around 7·18 δ (7H), whereas the hydroxyl proton appeared as an exchangeable singlet at 11·95 δ (1H). The two sets of ester methyl protons appeared as sharp singlets at 3·72 δ (3H) and 3·88 δ (3H). In addition, the spectrum of **21d** showed a pair of doublets centred around 4·55 δ (1H) (J = 5·0 Hz and 7·0 Hz) and a poorly resolved multiplet around 3·43 δ (2H). Of these, the pair of doublets at 4·55 δ is assigned to the C-4 proton, which is split by the two methylene protons, whereas the multiplet around 3·43 δ may be assigned to the methylene protons. Attempts to isolate a pure sample of **19d** were not successful.

Similarly, the reaction of 3,5 - dibromo - 2,2' - dihydroxychalcone **17e** with dimethyl acetylenedicarboxylate gave a 5% yield of dimethyl 3,5 - dibromo - 2' - hydroxychalcone - 2 - oxyfumarate **20e**, 13% yield of 2' - hydroxy - 3',5' - dibromoflavanone **22e** and a 74% yield of unresolved mixture of dimethyl 3,5 - dibromo - 2' - hydroxychalcone - 2 - oxymaleate **19e** and 2,3 - dicarbomethoxy - 4 - (o - hydroxyphenacyl) - 6,8 - dibromochrom - 2 - ene **21e**, consisting of 29% of **19e** and 71% of **21e** (by NMR). The NMR spectrum of the mixture of **19e** and **21e** showed a multiplet centred around 7·47 δ, assigned to the aromatic protons and two vinylic protons. The vinylic proton, of the maleate side chain appeared as a sharp singlet at 4·96 δ. The hydroxyl proton appeared as a sharp, exchangeable singlet at 11·95 δ, whereas the four sets of ester methyl protons appeared as four singlets at 4·05 δ, 3·98 δ, 3·78 δ and 3·72 δ. In addition, the spectrum showed two poorly resolved multiplets around 4·62 δ and 3·46 δ due to the C-4 proton and the methylene protons of the chromene, **21e**, respectively.

The reaction of a hydroxychalcone **17** with dimethyl acetylenedicarboxylate would be expected to proceed through a zwitterionic intermediate **18**, which may pick-up a proton to give the cis-addition product **19**, or the trans-addition product **20**. Another possible mode of reaction involves an intramolecular cyclization of the intermediate **18** to give the chromene derivative, **21**, as shown in Scheme 5. The formation of the flavanone derivatives, **22c,e** in these reactions can be rationalized in terms of an intramolecular cyclization of the starting 2'-hydroxychalcones in the presence of a base (Scheme 5).

EXPERIMENTAL

Melting points are uncorrected. IR spectra were recorded on a Perkin-Elmer Model 521 Infrared spectrometer and electronic spectra on a Cary-14 spectrophotometer. NMR spectra were recorded on either Varian A-60 or HA-100 NMR spectrometers.

Starting materials

Commercial samples of salicylaldehyde and o-hydroxyacetophenone were freshly distilled before use. 2-Hydroxychalcone,[13] m.p. 155–56°, 2 - hydroxy - 4' - methoxychalcone,[14] m.p. 149°, 2,2'-dihydroxychalcone,[11] m.p. 158–59°, 5 - chloro - 2,2' - dihydroxychalcone,[15] m.p. 192° and 3,5 - dibromo - 2,2' - dihydroxychalcone,[15] m.p. 201° were prepared by reported procedures.

Reaction of salicylaldehyde with dimethyl acetylenedicarboxylate

(A) *Using equimolar quantities of reactants* (1 : 1). A mixture of salicylaldehyde (4·9 g, 0·04 mol), dimethyl acetylenedicarboxylate (5·7 g, 0·04 mol) and anhydrous potassium carbonate (5·6 g, 0·04 mol) in dry benzene (50 ml) was stirred at room temperature for 30 hr. After diluting the reaction mixture by adding 50 ml of ether, it was washed with water and the organic layer dried over anhydrous sodium sulphate. Removal of the solvent under reduced pressure gave a light-brown viscous material, which was triturated with petroleum ether (b.p. 60–80°) to give 2·4 g (22%) of 2,3 - dicarbomethoxychrom - 2 - en - 4 - ol **7a**, m.p. 108°, after recrystallisation from methanol (Found: C, 59·11, H, 4·59. $C_{13}H_{12}O_6$ requires: C, 59·09; H, 4·54%). IR spectrum (KBr) ν_{max}: 3465 (O–H), 1722 (C=O, ester), 1700 (C=O, ester), 1667 (C=C), 1240 and 1228 cm^{-1} (C–O–C, alkyl aryl ether).

The mother-liquor of removal of **7a** was chromatographed over silica gel. Elution with a mixture of petroleum ether (b.p. 60–80°) and benzene (4 : 1) gave 20 mg (0·4%) of dimethyl fumarate, m.p. and m.m.p. 104°, after crystallisation from ethanol. Further elution of the silica column with a mixture (2 : 1) of petroleum ether and benzene gave 3·0 g of an yellow viscous material, which was purified separately. Continued elution of the column with benzene gave 220 mg (1%) of dimethyl (2,3 - dicarbomethoxychrom - 2 - en - 4 - yl) - oxalacetate **13a**, m.p. 226°, after recrystallisation from methanol (Found: C, 56·30; H, 4·70; MW, 406. $C_{19}H_{18}O_{10}$ requires: C, 56·16; H, 4·43%; MW, 406 (Mass spectrometry). IR spectrum (KBr) ν_{max}: 2964 (C–H), 2862 (C–H), 1750 (C=O, ester), 1734 (C=O, ester), 1708 (C=O, keto), 1648 (C=C), 1226 (C–O–C, alkyl aryl ether), 1124, 1090, 1052 and 976 cm^{-1}.

The yellow viscous mass (3·0 g) obtained earlier was separately chromatographed over silica gel. Elution with a mixture of petroleum ether and benzene (8 : 1) gave an additional amount (25 mg, 0·4%) of dimethyl fumarate, m.p. and m.m.p. 104°. Further elution of the silica column with a 3 : 1 mixture of petroleum ether and benzene gave 2·6 g of a yellow viscous material. Continued elution of the column with a mixture of petroleum ether and benzene (1 : 6) gave 100 mg (1%) of 2,3 - dicarbomethoxychrom - 3 - en - 2 - ol **8a**, m.p. 141°, after recrystallisation from methanol (Found: C, 59·10; H, 4·52. $C_{13}H_{12}O_6$ requires: C, 59·09; H, 4·59%). IR spectrum (KBr) ν_{max}: 3460 (O–H), 1731 (C=O, ester), 1704 (C=O, ester), 1630 (C=C), 1604 (C=C, aromatic), 1568, 1456, 1444, 1300, 1281, 1260, 1235, 1216 (C–O–C, alkyl aryl ether), 1141, 1118, 1048, 1002, 953, 944, 843, 785, 760 and 732 cm^{-1}. NMR spectrum (H_2SO_4): 8·73 δ (5H, m, ring protons), 4·52 δ (3H, s, C-2 ester methyl) and 4·43 δ (3H, s, C-3 ester methyl).

The yellow viscous mass (2·6 g) obtained in the second chromatograph was repeatedly chromatographed over silica gel to give 1·5 g (14%) of dimethyl o-formylphenoxyfumarate **4a**, m.p. 84°, after recrystallisation from a mixture of petroleum ether and benzene (1 : 2) (Found: C, 59·45; H, 4·70; MW, 264 (mass spectrometry). $C_{13}H_{12}O_6$ requires: C, 59·09; H, 4·54%, MW, 264). IR spectrum (KBr) ν_{max}: 3096 (C–H), 2969 (C–H), 1733 (C=O, ester), 1725 (C=O, ester), 1693 (C=O, aldehydic), 1658 (C=C), 1603 (C=C, aromatic), 1481, 1435, 1275, 1226 (C–O–C, alkyl aryl ether), 1202, 1180, 1160, 1115 and 1094 cm^{-1}. UV spectrum (CH_3OH) λ_{max}: 247 nm (ε, 13,300) and 308 (3,800).

The mother-liquor left behind after the isolation of **4a** was concentrated to remove all the solvent and the residual liquid (1 g) was distilled under vacuum to give 0·9 g (8%) of a light yellow liquid, b.p. 165–171° (bath temperature) (0·002 mm), consisting of a mixture of **4a** (40%) and dimethyl o-formylphenoxymaleate **5a** (60%) as identified by NMR (Found: C, 58·85; H, 4·85. $C_{13}H_{12}O_6$ requires: C, 59·09; H, 4·54%). IR spectrum (thin film) ν_{max}: 2960 (C–H), 1744 (C=O, ester), 1720 (C=O, ester), 1713 (C=O, ester), 1700 (C=O, ester), 1682 (C=O, aldehydic), 1648 and 1631 cm^{-1}. NMR spectrum (CCl_4): 10·63 δ (s, fumarate formyl), 10·40 δ (s, maleate formyl), 7·56 δ (m, aromatic), 6·87 δ (s, fumarate vinylic), 5·40 δ (s, maleate vinylic), 3·87 δ (m, ester methyl).

Treatment of salicylaldehyde with dimethyl acetylenedicarboxylate in refluxing benzene for 4 hr and work-up in the usual manner gave a brown viscous material, which was chromatographed over silica gel to give a 23% yield of **8a**, m.p. and m.m.p. 141°, 34% yield of **4a**, m.p. and m.m.p. 84° and 9% yield of a mixture of **4a** and **5a**, b.p. 166–173° (bath temperature) (0·002 mm), consisting of 88% of **4a** and 12% **5a**, as identified by NMR.

Salicylaldehyde was also treated with dimethyl acetylenedicarboxylate in acetone for 30 hr at room temperature. Work-up of the mixture as in the earlier cases gave a 10% yield of **7a**, m.p. and m.m.p. 108°, 8% yield of **8a**, m.p. and m.m.p. 141° and a 29% yield of a mixture of **4a** and **5a** isolated through their 2,4-dinitrophenylhydrazones, m.p. 239–241°, after recrystallisation from a mixture of chloroform and methanol (2:1).

(B) *Using excess of dimethyl acetylenedicarboxylate* (1:2). A mixture of salicylaldehyde (2·5 g, 0·02 mol), dimethyl acetylenedicarboxylate (5·7 g, 0·04 mol) and anhydrous potassium carbonate (2·8 g, 0·02 mol) in 50 ml of dry benzene was refluxed for 4 hr. Work-up of the reaction mixture in the usual manner gave 6·0 g of a dark red, viscous mass which was chromatographed over silica gel. Elution with benzene gave 3·0 g of a yellow viscous mass which was fractionally crystallised from methanol to give 350 mg (7%) of **8a**, m.p. and m.m.p. 141° and 420 mg (5%) of dimethyl (2,3 - dicarbomethoxychrom - 3 - en) - 2 - oxyfumarate **10a**, m.p. 123° after recrystallisation from methanol (Found: C, 56·34; H, 4·63. MW, 406. $C_{19}H_{18}O_{10}$ requires: C, 56·16; H, 4·43%; MW, 406 (Mass spectrometry). IR spectrum (KBr) ν_{max}: 2960 (C–H), 1756 (C=O, ester), 1735 (C=O, ester), 1705 (C=O, ester), 1620 (C=C), 1600 (C=C, aromatic), 1287 and 1257 cm^{-1}. UV spectrum (CH_3OH) λ_{max}: 238 nm (ϵ, 2,300), 285 (8,600), 294 (sh, 7,400) and 350 (3,700). UV spectrum (aqueous methanolic sulphuric acid) λ_{max}: 230 nm, 278, 288 (sh) and 325. UV spectrum (H_2SO_4) λ_{max}: 265 nm (ϵ, 24,900) and 348 (13,600).

Nickel peroxide oxidation of 2,3-*dicarbomethoxychrom*-2-*en*-4-*ol* **7a**

A mixture of 2,3 - dicarbomethoxychrom - 2 - en - 4 - ol **7a** (0·23 g, 0·9 mmol) and nickel peroxide (1·2 g) was stirred in refluxing benzene for 6 hr. Removal of the inorganic material and concentration of the organic layer under vacuum gave 0·2 g of a light yellow viscous mass which gave 110 mg (50%) of 2,3-dicarbomethoxychromone **16**, m.p. 138°, after recrystallisation from methanol (Found: C, 59·75; H, 3·90. $C_{13}H_{10}O_6$ requires: C, 59·54; H, 3·81%). IR spectrum (KBr) ν_{max}: 1742 (C=O, ester), 1732 (C=O, ester), 1648 (C=O, keto), 1631 (C=C) and 1246 cm^{-1} (C–O–C of alkyl aryl ether).

The mother-liquor was concentrated and chromatographed over silica gel. Elution with benzene gave a further yield of **16** (30 mg, 11%), m.p. and m.m.p. 138°.

2,3-*Dinitrophenylhydrazone of dimethyl o-formylphenoxyfumarate* **4a**

To a soln of dimethyl o-formylphenoxyfumarate **4a** (10 mg, 0·04 mmol) in 5 ml of methanol was added an excess of 2,4-dinitrophenylhydrazine reagent to give an orange solid (14 mg, 83%), m.p. 241°, after crystallisation from a mixture of chloroform and methanol (2:1). (Found: C, 51·50; H, 3·41; N, 13·08. $C_{19}H_{16}N_4O_9$ requires: C, 51·35; H, 3·60; N, 12·61%). IR spectrum (KBr) ν_{max}: 1728 (C=O, ester), 1715 (C=O, ester), 1610 (C=C), 1202 (C–O–C) and 1130 cm^{-1}. IR spectrum ($CHCl_3$) ν_{max}: 3300 cm^{-1} (N–H). UV spectrum (CH_2Cl_2) λ_{max}: 384 nm (ϵ, 31,200).

Rearrangement of 2,3 - *Dicarbomethoxychrom* - 2 - *en* - 4 - *ol* **7a** *to* 2,3 - *dicarbomethoxychrom* - 3 - *en* - 2 - *ol* **8a**

(A) *Using aqueous methanolic hydrogen chloride.* A soln of **7a** (50 mg, 0·2 mmol) in 20 ml of 90% methanol was saturated with HCl gas. Removal of the solvent under reduced pressure gave a pale yellow viscous mass which was dissolved in benzene and the benzene-solution washed with water and dried over anhydrous sodium sulphate. Removal of the solvent under vacuum gave a viscous liquid which on trituration with methanol gave 42 mg (80%) of 2,3 - dicarbomethoxychrom - 3 - en - 2 - ol **8a**, m.p. 141° (m.m.p.)

(B) *Using silica gel.* A soln of **7a** (110 mg, 0·4 mmol) in 5 ml of benzene was adsorbed on a silica gel column and left for 24 hr. Elution of the column with benzene gave 97 mg (88%) of **8a**, m.p. and m.m.p. 141°.

(C) *Attempted rearrangement using anhydrous potassium carbonate.* A soln of **7a** (50 mg, 0·02 mmol) in 10 ml of benzene was refluxed with anhydrous potassium carbonate (0·2 g, 1·5 mmol) for 4 hr. Work-up of the reaction mixture in the usual manner gave a viscous liquid which gave on trituration with methanol, 35 mg (70%) of the unchanged starting material **7a**, m.p. and m.m.p. 108°. TLC (neutral alumina) of the mother-liquor did not show the presence of any rearranged product, **8a**.

(D) *Using salicylaldehyde in the presence of anhydrous potassium carbonate.* A mixture of **7a** (110 mg, 0·4 mmol), salicylaldehyde (50 mg, 0·4 mmol) and anhydrous potassium carbonate (50 mg, 0·4 mmol) was refluxed in benzene (10 ml) for 4 hr. Work-up of the reaction mixture in the usual manner gave a product which on trituration with methanol gave 50 mg (45%) of the unchanged starting chromenol, **7a**, m.p. and m.m.p. 108°. The mother-liquor was concentrated and triturated with a mixture of benzene and petroleum ether (1:2) to give 30 mg (20%) of **8a**, m.p. and m.m.p. 141°.

Generation of 2,3-*dicarbomethoxybenzopyrylium ion* **14a** *and its reaction with methanol*

(A) *From* 2,3 - *dicarbomethoxychrom* - 2 - *en* - 4 - *ol* **7a**. A soln of **7a** (130 mg, 0·5 mmol) in 5 ml of dry methanol was refluxed for 12 hr with 0·1 N methanolic toluene - p - sulphonic acid (2·5 ml). The reaction mixture was cooled and neutralised with dry pyridine. After removal of the solvent under vacuum, the mixture was extracted with ether and the ether-extract washed with water. Removal of the solvent from the ether-extract gave 130 mg (99%) of 2 - methoxy - 2,3 - dicarbomethoxychrom - 3 - ene **15a** m.p. 89°, after recrystallisation from methanol (Found: C, 60·80; H, 5·04. $C_{14}H_{14}O_6$ requires: C, 60·43; H, 5·04%). IR spectrum (KBr) ν_{max}: 2956 (C–H), 2843 (C–H), 1760 (C=O, ester), 1708 (C=O, ester), 1627 (C=C), 1292 (C–O–C, dialkyl ether), 1252 and 1216 cm^{-1} (C–O–C, alkyl aryl ether). UV spectrum (CH_3OH) λ_{max}: 233 nm (ϵ, 15,000), 282 (14,800), 288 (sh, 14,200) and 329 (5,800). UV spectrum (H_2SO_4) λ_{max}: 265 nm (ϵ, 24,700) and 348 (13,100). NMR spectrum ($CDCl_3 + D_2O + H_2SO_4$ (one drop)): 7·96 δ (1H, s, C_4–H), 7·32 δ (4H, m, aromatic), 3·98 δ (3H, s, ester methyl) and 3·90 δ (3H, s, ester methyl). NMR spectrum (H_2SO_4): 8·73 δ (5H, m, ring protons), 4·52 δ (3H, s, C-2 ester methyl), 4·43 δ (3H, s, C-3 ester methyl) and 4·26 δ (3H, s, methyl protons of methanol).

(B) *From* 2,3 - *dicarbomethoxychrom* - 3 - *en* - 2 - *ol* **8a**. A soln of **8a** (130 mg, 0·5 mmol) in 10 ml of dry methanol was acidified with a drop of 98% sulphuric acid and the mixture was refluxed for 12 hr. Work-up of the reaction mixture as in the earlier case gave a product which on fractional crystallisation from methanol gave 77 mg (68%) of 2 - methoxy - 2,3 - dicarbomethoxychrom - 3 - ene **15a**, m.p. and m.m.p. 89° and 11 mg of the starting chromenol, **8a**, m.p. and m.m.p. 141°.

Reaction of 2,3 - *dicarbomethoxychrom* - 2 - *en* - 4 - *ol* **7a** *with dimethyl sulphate*

A mixture of **7a** (130 mg, 0·5 mmol) and dimethyl sulphate (73 mg, 0·5 mmol) was refluxed for 2 hr in dry acetone (10 ml) containing anhydrous potassium carbonate (100 mg, 0·75 mmol). Work-up of the reaction mixture in the usual manner gave 40 mg (29%) of **15a**, m.p. and m.m.p. 89°.

Attempted reaction of 2,3 - *dicarbomethoxychrom* - 2 - *en* - 4 - *ol* **7a** *with diazomethane*

To a soln of **7a** (130 mg, 0·5 mmol) in 10 ml of dry ether was added an excess of a solution of diazomethane in ether. The reaction mixture was allowed to stand overnight and the solvent was removed under vacuum to give 125 mg (96%) of the unchanged starting material, m.p. and m.m.p. 108°.

Reaction of 2,3 - *dicarbomethoxychrom* - 3 - *en* - 2 - *ol* **8a** *with diazomethane*

To a soln of **8a** (130 mg, 0·5 mmol) in 10 ml of dry ether was added an excess of a solution of diazomethane in ether. The reaction mixture was allowed to stand over-night and the solvent removed under vacuum to give a product which was fractionally crystallised from methanol to give 28 mg (20%) of **15a**, m.p. and m.m.p. 89° and 60 mg of the unchanged starting material **8a**, m.p. and m.m.p. 141°.

Attempted reaction of 2,3, - *dicarbomethoxychrom* - 2 - *en* - 4 - *ol* **7a** *with dimethyl acetylenedicarboxylate*

A mixture of **7a** (130 mg, 0·5 mmol), dimethyl acetylenedicarboxylate (100 mg, 0·7 mmol) and anhydrous potassium carbonate (200 mg, 1·5 mmol) was refluxed for 4 hr in 10 ml of dry benzene. Work-up of the reaction mixture in the usual manner gave a viscous mass (130 mg) which was triturated with petroleum ether. The petroleum ether-insoluble portion was crystallised from a mixture of petroleum ether and benzene (2 : 1) to give 80 mg (61%) of unchanged **7a**, m.p. 108° (m.m.p.). The petroleum ether-soluble portion was chromatographed over a silica gel column to give 42 mg (31%) of **8a**, m.p. and m.m.p. 141°.

Reaction of 2,3 - *dicarbomethoxychrom* - 3 - *en* - 2 - *ol* **8a** *with dimethyl acetylenedicarboxylate*

A mixture of **8a** (260 mg, 1 mmol), dimethyl acetylenedicarboxylate (280 mg, 2 mmol) and anhydrous potassium carbonate (0·3 g) in dry benzene (15 ml) was refluxed for 4 hr. The reaction mixture was worked up in the usual manner to give 450 mg of a red viscous mass which was treated with petroleum ether to remove any unchanged dimethyl acetylenedicarboxylate. The petroleum ether-insoluble portion was recrystallised from a mixture of petroleum ether and benzene (1 : 1) to give 140 mg (37%) of 2,3 - 12 - tricarbomethoxychrom - 3,4 - eno[2,3 - b]pyrone **11a**, m.p. 147° (Found: C, 57·55; H, 3·98. $C_{18}H_{14}O_9$ requires: C, 57·75; H, 3·98%). IR spectrum (KBr) ν_{max}: 1757 (C=O, ester), 1748 (C=O, ester), 1668 (C=O, keto) 1626 (C=C), 1616 (C=C), 1284, 1260, 1230 and 1223 cm^{-1}. UV spectrum (CH_3OH) λ_{max}: 241 nm (ϵ, 11,900), 301 (11,800) and 352 (9,300). UV spectrum (H_2SO_4) λ_{max}: 264 nm (ϵ, 20,800) and 352 (10,600).

The mother-liquor was concentrated and chromatographed over silica gel. Elution with benzene gave a viscous liquid mass which was triturated with a mixture of petroleum ether and benzene (2 : 1) to give 30 mg of unchanged starting material **8a**, m.p. and m.m.p. 141°. No other compound could be isolated, even on further elutions with more polar solvents.

Attempted nickel peroxide oxidation of dimethyl (2,3 - *dicarbomethoxychrom* - 3 - *en* - 4 - *yl*) - *oxalacetate* **13a**

A mixture of **13a** (50 mg, 0·12 mmol) and nickel peroxide (0·5 g) was stirred in refluxing benzene (15 ml) for 4 hr. Removal of the unchanged nickel peroxide and the solvent gave 48 mg of the unchanged starting material, **13a**, m.p. 226° (m.m.p.).

Reaction of o-hydroxyacetophenone **1b** *with dimethyl acetylenedicarboxylate*

A mixture of **1b** (1·36 g, 0·01 mol), dimethyl acetylenedicarboxylate (1·42 g, 0·01 mol) and anhydrous potassium carbonate (1·4 g, 0·01 mol) was stirred in dry acetone (30 ml) at room temperature (30°) for 30 hr. Work-up as in the earlier cases gave a light yellow viscous mass, which was triturated with methanol to give 1·45 g (67%) of 2,3 - dicarbomethoxy - 4 - methylchrom - 2 - en - 4 - ol **7b**, m.p. 108·5, after recrystallisation from a mixture of benzene and petroleum ether (1 : 2) (Found: C, 60·98; H, 5·44. $C_{14}H_{14}O_6$ requires: C, 60·43; H, 5·04%.) IR spectrum (KBr) ν_{max}: 3416 (O–H), 2991 (C–H), 2966 (C–H), 1720 (C=O, ester), 1700 (C=O, ester), and 1646 cm^{-1} (C=C).

The mother-liquor, after the removal of **7b** was concentrated and the solid separated out was fractionally crystallised from a mixture of benzene and petroleum ether (1 : 1) to give 100 mg (5%) of 2,3 - dicarbomethoxy - 4 - methylchrom - 3 - en - 2 - ol **8b**, m.p. 143–144° (Found: C, 60·91; H, 5·48. $C_{14}H_{14}O_6$ requires: C, 60·43; H, 5·04%.) IR spectrum (KBr) ν_{max}: 3456 (O–H), 2972 (C–H), 1737 (C=O, C_2-carbomethoxy), 1694 (C=O, C_3-carbomethoxy), 1622 (C=C) and 1602 cm^{-1} (C=C, aromatic). UV spectrum (CH_3OH) λ_{max}: 218 nm (ϵ, 13,600), 226 (13,850) and 316 (6,800). UV spectrum (98%, H_2SO_4) λ_{max}: 221 nm (ϵ, 15,200), 259 (22,400) and 347 (12,650). NMR spectrum (98% H_2SO_4): 8·76 δ (4H, m, aromatic), 4·37 δ (6H, s, two sets of ester methyls) and 3·35 δ (3H, s, C-4 methyl).

The mother-liquors left behind after the removal of **7b** and **8b** were combined together and chromatographed over silica gel. Elution with a mixture of petroleum ether and benzene (8 : 1) gave 250 mg of unchanged dimethyl acetylenedicarboxylate, identified by its IR spectrum. Further elution of the column with a mixture of benzene and petroleum ether (3 : 1) gave 300 mg of unchanged **1b**, identified by comparison with an authentic sample. Continued elution of the column with a mixture of benzene and petroleum ether (10 : 1) gave 150 mg of a yellow liquid (A), which was worked up separately. Further elution of the silica column with a mixture of benzene and ethyl acetate (6 : 1) gave 400 mg of a viscous material which on trituration with methanol gave a second crop of **8b** (140 mg, 7%), m.p. 143–144° (m.m.p.).

Repeated chromatography of the yellow liquid (A) on an alumina column using benzene gave 110 mg (5%) of mixture of **4b** and **5b**, b.p. 160–170° (bath temperature) (0·05 mm) (Found: C, 60·81; H, 4·96. $C_{14}H_{14}O_6$ requires: C, 60·43; H, 5·04%.) IR spectrum (KBr) ν_{max}: 2960 (C–H), 1746 (C=O, ester), 1736 (C=O, ester), 1726 (C=O, ester), 1716 (C=O, ester), 1708 (C=O, keto) and 1627 cm^{-1} (C=C). UV spectrum (CH_3OH) λ_{max}: 226 nm (ϵ, 9,400).

In a repeat run, a mixture of **1b** (1·36 g, 0·01 mol), dimethyl acetylenedicarboxylate (1·42 g, 0·01 mol) and anhydrous potassium carbonate (1·4 g, 0·01 mol) was refluxed in acetone (50 ml) for 6 hr and worked up as in the earlier case to give 1·4 g (50%) of **7b**, m.p. 108·5° (m.m.p.) and 57 mg (21%) of **8b**, m.p. 143–144° (m.m.p.).

Isomerization of 2,3 - *dicarbomethoxy* - 4 - *methylchrom* - 2 - *en* - 4 - *ol* **7b**

(A) *Under acid conditions.* To a soln of the 4-chromenol **7b** (280 mg, 1 mmol) in 5 ml of 98% sulphuric acid was added 50 ml of water and the organic portion was extracted with ether. The ether-extract was washed with water, dried over anhydrous sodium sulphate and the solvent removed under vacuum to give a yellow viscous liquid. Trituration with a mixture of petroleum ether and benzene (2 : 1) gave 230 mg (82%) of **8b**, m.p. 143–144° (m.m.p.), after recrystallisation from methanol.

In another experiment, a soln of **7b** (280 mg, 1 mmol) in 25 ml of chloroform was shaken for 4 hr, with 50 ml of hydrochloric acid (1%). The organic layer was washed with water and dried over anhydrous sodium sulphate. Removal of the solvent under vacuum gave 271 mg (96%) of **8b**, m.p. 143–144° (m.m.p.), after recrystallisation from methanol.

(B) *Under thermal conditions.* A soln of 280 mg (1 mmol) of **7b** in 20 ml of benzene was refluxed for 48 hr. Removal of the solvent under vacuum gave a product which was chromatographed over alumina. Elution with benzene gave 110 mg (40%) of **8b**, m.p. 143–144° (m.m.p.), after recrystallisation from methanol.

In a separate experiment, 600 mg (2·2 mmol) of **7b** was kept at room temperature for nearly 12 months, during which period, the compound changed to a brown, semi-solid mass. Work-up of this mixture by chromatographing over alumina and using benzene as eluent gave 450 mg (75%) of **8b**, m.p. 143–144° (m.m.p.).

Reaction of 2-hydroxychalcone with dimethyl acetylenedicarboxylate

A mixture of 2-hydroxychalcone **17a** (1·68 g, 7·5 mmol), dimethyl acetylenedicarboxylate (1·1 g, 7·5 mmol) and anhydrous potassium carbonate (1 : 1 g, 8 mmol) was refluxed in dry benzene (30 ml) for 4 hr. The organic layer was washed with water and dried over anhydrous sodium sulphate. Removal of the solvent under vacuum gave a light brown, viscous liquid which on trituration with methanol gave 1 g (46%) of dimethyl chalcone - 2 - oxyfumarate **20a**, m.p. 155°, after recrystallisation from a mixture of methanol and chloroform (5 : 1) (Found: C, 68·71; H, 4·92. $C_{21}H_{18}O_6$ requires: C, 68·85; H, 4·92%). IR spectrum (KBr) ν_{max}: 3088 (=C–H), 3056 (=C–H), 3002 (C–H, aromatic), 2960 (C–H, aliphatic), 1730 (C=O, ester), 1713 (C=O, ester), 1658 (C=O, keto), 1648 (C=C) and 1640 cm^{-1} (C=C). UV spectrum (CH_3OH) λ_{max}: 222 nm (ϵ, 20,700), 234 (sh, 18,800) and 296 (19,400).

The mother-liquor, after removal of **20a** was chromatographed over a silica gel column. Elution with a mixture of petroleum ether and benzene (1 : 3) gave 1 g of an yellow viscous mass which was worked up separately. Further elution of the silica column with a mixture of benzene and ethyl acetate (3 : 1) gave 350 mg of the unchanged 2-hydroxychalcone **17a**, m.p. 155–156° (m.m.p.).

The yellow viscous mass (1 g), obtained earlier through chromatographic separation was triturated with methanol to give a second fraction of **20a** (180 mg, 8%), m.p. 155° (m.m.p.). The methanolic mother-liquor was concentrated under vacuum and later chromatographed over silica gel using benzene as eluent to give 560 mg (26%) of dimethyl chalcone - 2 - oxymaleate **19a**, as a viscous yellow liquid (Found: C, 68·66; H, 4·92. $C_{21}H_{18}O_6$ requires: C, 68·85; H, 4·92%). IR spectrum (CCl_4) ν_{max}: 3080 (=C–H), 3044 (=C–H), 3008 (C–H, aromatic), 2962 (C–H, aliphatic, 1748 (C=O, ester), 1716 (C=O, ester), 1716 (C=O, ester), 1685 (C=O, keto), 1632 (C=C) and 1602 cm^{-1} (C=C). UV spectrum (CH_3OH) λ_{max}: 218 nm (ϵ, 13,400), 240 (11,300), 272 (9,700) and 289 (9,000).

Attempted cyclization of dimethyl chalcone - 2 - oxyfumarate **20a**

(A) *Using methanolic hydroxen chloride.* A soln of **20a** (180 mg, 0·5 mmol) in absolute methanol (10 ml) was saturated with dry hydrogen chloride gas and then refluxed for 24 hr. Removal of the solvent under vacuum gave a viscous mass, which on trituration with cold ethanol gave 170 mg (94%) of unchanged **20a**, m.p. 155° (m.m.p.). No other product could be isolated from this reaction.

(B) *Using orthophosphoric acid.* A mixture of **20a** (90 mg, 0·25 mmol) and orthophosphoric acid (5 ml) was heated around 140° for 4 hr. Treatment of the reaction mixture with water and work-up in the usual manner gave 82 mg (91%) of unchanged **20a**, m.p. 155° (m.m.p.).

(C) *Using sodium methoxide in methanol.* A soln of **20a** (180 mg, 0·5 mmol) in 10 ml of 2% methanolic sodium methoxide was refluxed for 10 hr. The reaction mixture, after acidification with 10% hydrochloric acid was cooled to give 165 mg (92%) of the unchanged starting material **20a**, m.p. 155° (m.m.p.).

(D) *Under thermal conditions.* A soln of **20a** (90 mg, 0·25 mmol) in 5 ml of dry toluene was refluxed for 14 hr. TLC showed that the reaction mixture contained only **20a**. The solvent was removed under vacuum, and the residue was taken up in 10 ml of diphenyl ether. After refluxing in diphenyl ether for 12 hr, the solvent was removed under vacuum and the brown viscous material was triturated with a mixture of benzene and petroleum ether (1:1) to give 68 mg (75%) of unchanged **20a**, m.p. 154–155° (m.m.p.). The mother-liquor was concentrated and chromatographed over silica gel. Elution with different solvents did not give any identifiable product.

Reaction of 2 - hydroxy - 4′ - methoxychalcone **17b** *with dimethyl acetylenedicarboxylate*

A mixture of 1·9 g (7·5 mmol) of **17b**, 1·1 g (7·5 mmol) of dimethyl acetylenedicarboxylate and 1·1 g (8 mmol) of anhydrous potassium carbonate was refluxed in 30 ml of dry benzene for 4 hr. Work-up of the reaction mixture as in the earlier cases gave 2·9 g of a yellow viscous material which was triturated with methanol to give 1·1 g (51%) of dimethyl 4′ - methoxychalcone - 2 - oxyfumarate **20b**, m.p. 125°, after recrystallisation from methanol (Found: C, 66·26; H, 4·89. $C_{22}H_{20}O_7$ requires: C, 66·67; H, 5·05%). IR spectrum (KBr) ν_{max}: 3016 (C–H), 2960 (C–H), 1710 (C=O, ester), 1707 (C=O, ester), 1648 (C=O, keto), 1644 (C=C) and 1600 cm^{-1} (C=C). NMR spectrum ($CDCl_3$): 7·75 δ (10H, m, aromatic and vinylic protons, H_a and H_b), 6·80 δ (1H, s, vinylic proton, H_c), 3·98 δ (3H, s, ester methyl), 3·82 δ (3H, s, ester methyl) and 3·79 δ (3H, s, C-4′ methoxy).

The mother-liquor (1·8 g), after the removal of **20b** was chromatographed over silica gel. Elution with a mixture of petrolum ether and benzene (1:3) gave a second crop of **20b** (200 mg, 9%), m.p. 125° (m.m.p.). Further elution of the silica column with benzene gave 0·62 g of a yellow liquid which was further purified by repeated chromatography over silica gel to give 0·5 g (23%) of dimethyl 4′ - methoxychalcone - 2 - oxymaleate **19b** (Found: C, 66·60; H, 5·10. $C_{22}H_{20}O_7$ requires: C, 66·67; H, 5·05%). IR spectrum (CCl_4) ν_{max}: 3006 (C–H), 2962 (C–H), 1748 (C=O, ester), 1721 (C=O, ester), 1660 (C=O, keto), 1632 (C=C) and 1598 cm^{-1} (C=C). NMR spectrum ($CDCl_3$): 7·62 δ (10H, m, aromatic vinylic H_a, H_b), 5·27 δ (1H, s, vinylic), 4·0 δ (3H, s, ester methyl), 3·88 δ (3H, s, ester methyl) and 3·70 δ (3H, s, C-4′ methoxy).

Continued elution of the silica column with a mixture (2:1) of benzene and ethyl acetate gave 0·5 g of the unchanged 2 - hydroxy - 4′ - methoxychalcone **17b**, m.p. 149° (m.m.p.).

Reaction of 2,2′-dihydroxychalcone **17c** *with dimethyl acetylenedicarboxylate*

A mixture of 2,2′-dihydroxychalcone **17c** (1·5 g, 6 mmol), dimethyl acetylenedicarboxylate (0·85 g, 6 mmol) and anhydrous potassium carbonate (1·8 g, 14 mmol) was refluxed in dry benzene (50 ml) for 4 hr. Work-up of the reaction mixture as in the earlier cases gave 2·2 g of a viscous mass which on trituration with methanol gave 0·9 g (51%) of dimethyl 2′ - hydroxychalcone - 2 - oxyfumarate **20c**, m.p. 170–171°, after crystallisation from a mixture of benzene and methanol (2:1) (Found: C, 66·18; H, 4·63. $C_{21}H_{18}O_7$ requires: C, 65·97; H, 4·71%). IR spectrum (KBr) ν_{max}: 3080 (OH, hydrogen-bonded), 3014 (C–H), 2954 (C–H), 1732 (C=O, ester), 1712 (C=O, ester), 1648 (C=O, keto), 1640 (C=C) and 1632 cm^{-1} (C=C). NMR spectrum ($CDCl_3$): 12·98 δ (1H, s, exchangeable with D_2O, OH), 7·80 δ (10H, m, aromatic and the vinylic protons, H_a and H_b), 6·87 δ (1H, s, vinylic proton, H_c), 3·85 δ (3H, s, ester methyl) and 3·81 δ (3H, s, ester methyl).

The mother-liquor, obtained after the removal of **20c** was chromatographed over silica gel. Elution with benzene gave 550 mg of a yellow liquid which was repeatedly chromatographed over silica gel to give 480 mg (27%) of dimethyl 2′ - hydroxychalcone - 2 - oxymaleate **19c** (Found: C, 66·08; H, 4·76. $C_{21}H_{18}O_7$ requires: C, 65·97; H, 4·71%). IR spectrum (KBr) ν_{max}: 3056 (O–H), 3024 (C–H), 2956 (C–H), 1736 (C=O, ester), 1711 (C=O, ester), 1658 (C=O, keto) and 1635 cm^{-1} (C=C). NMR spectrum ($CDCl_3$): 12·83 δ (1H, s, exchangeable with D_2O, OH), 7·72 δ (10H, m, aromatic and the vinylic protons, H_a and H_b), 5·29 δ (1H, s, vinylic proton, H_c), 4·04 δ (3H, s, ester methyl) and 3·77 δ (3H, s, ester methyl).

Further elution of the silica column with a mixture of benzene and ethyl acetate (1:3) gave 96 mg (9%) of 2′-hydroxyflavanone **22c**, m.p. 166–167° (lit.[9] m.p. 165–165·5°), after recrystallisation from a mixture of benzene and ethyl acetate (2:1) (Found: C, 75·04; H, 4·88. $C_{15}H_{12}O_3$ requires: C, 75·00; H, 5·00%). IR spectrum (KBr) ν_{max}: 3196 (O–H), 1660 (C=O), 1656 (C=O) and 1596 cm^{-1} (C=C, aromatic). UV spectrum (CH_3OH) λ_{max}: 224 nm (ϵ, 18,300), 252 (8,900), 275 (sh, 3,250), 281 (3,400) and 322 (3,540). NMR spectrum (CD_3COCD_3): 8·76 δ (1H, exchangeable with D_2O, OH), 8·15 δ (1H, pair of doublets, C-5H, J = 9·0 Hz and 1·8 Hz), 7·78 δ (3H, m, C-6, C-7 and C-8 H), 7·25 δ (4H, C-3′, C-5′ and C-6′ H), 6·05 δ (1H, pair of doublets, C-2 H, J = 10·0 Hz and 6·0 Hz), 3·18 δ (2H, m, methylene).

Furher elution of the silica column with a mixture of benzene and ethyl acetate (3:1) gave 400 mg of unchanged 2,2′-dihydroxychalcone **17c**, m.p. 158–9° (m.m.p.).

Reaction of 5 - chloro - 2,2′ - dihydroxychalcone **17d** *with dimethyl acetylendicarboxylate*

A mixture of 5 - chloro - 2,2′ - dihydroxychalcone **17d** (0·7 g, 2·5 mmol), dimethyl acetylenedicarboxylate (0·36 g, 2·5 mmol) and anhydrous potassium carbonate (0·7 g, 5 mmol) was refluxed in 30 ml of dry benzene for 10 hr. Work-up of the reaction mixture in the usual manner gave 1·05 g of a viscous material which on trituration with methanol gave 220 mg (27%) of dimethyl 5 - chloro - 2′ - hydroxychalcone - 2 - oxyfumarate **20d**, m.p. 182–183°, after recrystallisation from a mixture of chloroform and methanol (1:2) (Found: C, 60·70; H, 4·50. $C_{21}H_{17}ClO_7$ requires: C, 60·50; H, 4·08%). IR spectrum (KBr) ν_{max}: 3088 (O–H), 3000 (C–H), 2960 (C–H), 1729 (C=O, ester), 1714 (C=O, ester), 1650 (C=O, keto) and 1635 cm^{-1} (C=C). NMR spectrum ($CDCl_3$): 13·05 δ (1H, s, exchangeable with D_2O, OH), 7·65 δ (9H, m, aromatic and the vinylic protons, H_a and H_b), 6·92 δ (1H, s, vinylic), 3·89 δ (3H, s, ester methyl) and 3·85 δ (3H, s, ester methyl).

The mother-liquor was chromatographed over silica gel and elution with a mixture of petroleum ether and benzene (1:2) gave 520 mg (63%) of a mixture (1:1) of dimethyl 5 - chloro - 2′ - hydroxychalcone - 2 - oxymaleate **19d** and 2,3 - dicarbomethoxy - 4 - (o - hydroxyphenacyl) - 6 - chlorochrom - 2 - ene **21d** (Found: C, 60·55; H, 4·05. $C_{21}H_{17}ClO_7$ requires: C, 60·50; H, 4·08%). IR spectrum (CCl_4) ν_{max}: 2958 (C–H), 1756 (C=O, ester), 1748 (C=O, ester), 1728 (C=O, ester), 1698 (C=O, ester), and 1640 cm^{-1} (C=O).

Further elution of the silica column with a mixture of benzene and ethyl acetate (3:1) gave 200 mg of the unchanged starting material, **17d**, m.p. 191–192° (m.m.p.).

Repeated chromatography of the mixture of **19d** and **21d** resulted in the isolation of 60 mg of a pure sample of **21d** (Found:

C, 60·13; H, 4·16. $C_{21}H_{17}ClO_7$ requires: C, 60·50; H, 4·08%). IR spectrum (CCl_4) ν_{max}: 2960 (C–H), 2928 (C–H), 2870 (C–H), 1750 (C=O, ester), 1720 (C=O, ester) 1640 (C=O) and 1610 cm^{-1} (C=C).

Reaction of 3,5 *- dibromo -* 2,2′ *- dihydroxychalcone* **17e** *with dimethyl acetylenedicarboxylate*

A mixture of **17e** (1·59 g, 4 mmol), dimethyl acetylenedicarboxylate (580 mg, 4 mmol) and anhydrous potassium carbonate (1·2 g, 9 mmol) was refluxed in dry benzene (30 ml) for 4 hr. Work-up of the reaction mixture in the usual manner gave a viscous mass which was triturated with benzene to give 0·85 g of unchanged starting material, **17e**, m.p. 201° (m.m.p.).

The mother-liquor was concentrated and chromatographed over silica gel. Elution with a mixture of petroleum ether and benzene (4:1) gave 300 mg of unchanged dimethyl acetylenedicarboxylate, identified from its IR spectrum. Further elution of the silica column with a mixture of petroleum ether and benzene (2:1) gave an additional 50 mg of the unchanged starting material, **17e**, m.p. 198–200° (m.m.p.).

Subsequent elution of the silica column with mixture of petroleum ether and benzene (1:3) gave 50 mg (5%) of dimethyl 3,5 - dibromo - 2′ - hydroxychalcone - 2 - oxyfumarate **20e**, m.p. 163–164°, after recrystallisation from methanol (Found: C, 47·15; H, 3·02. $C_{21}H_{16}Br_2O_7$ requires: C, 46·67; H, 2·96%). IR spectrum (KBr) ν_{max}: 3076 (O–H), 2948 (C–H), 1718 (C=O, ester), 1694 (C=O, ester), 1648 (C=O, keto) and 1632 cm^{-1} (C=C). NMR spectrum ($CDCl_3$): 12·71 δ (1H, s, exchangeable with D_2O, H-bonded OH), 7·67 δ (8H, m, aromatic and vinylic protons, H_a and H_b), 6·52 δ (1H, s, vinylic proton, H_c) and 3·87 δ (6H, two overlapping singlets, two sets of ester methyl protons).

Continued elution of the silica column with benzene gave 880 mg of a yellow viscous liquid which on trituration with benzene gave 90 mg (13%) of 2′ - hydroxy - 3′,5′ - dibromoflavanone **22e**, m.p. 196–7°, after recrystallisation from a mixture of benzene and petroleum ether (5:1) (Found: C, 45·10; H, 2·71. $C_{15}H_{10}Br_2O_3$ requires: C, 45·23; H. 2·51%). IR spectrum (KBr) ν_{max}: 3196 (O–H), 1676 (C=O) and 1666 cm^{-1} (C=O). UV spectrum (CH_3OH) λ_{max}: 222 nm (ϵ, 45,750), 252 (17,300), 287 (6,100) and 318 (6,200). NMR spectrum ($CDCl_3$): 7·87 δ (6H, m, aromatic), 6·10 δ (1H, s, exchangeable with D_2O, OH), 5·87 δ (1H, m, C-2 H), 3·05 δ (2H, m, C-3 methylene).

The mother-liquor, after the removal of **22e** was rechromatographed over silica gel to give 0·7 g (74%) of a mixture (2:5) of dimethyl 3,5 - dibromo - 2′ - hydroxychalcone - 2 - oxymaleate **19e** and 2,3 - dicarbomethoxy - 4 - (o - hydroxyphenacyl) - 6,8 - dibromochrom - 2 - ene **21e**. (Found: C, 46·50; H, 2·85. $C_{21}H_{16}Br_2O_7$ requires: C, 46·67; H, 2·96%). IR spectrum (CCl_4) ν_{max}: 3090 (O–H), 3040 (=C–H), 2952 (C–H), 1756 (C=O, ester), 1744 (C=O, ester), 1728 (C=O, ester), 1642 (C=O, keto) and 1615 cm^{-1} (C=C).

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