Photochemical Reactions. Part V.[1] Photoinduced Cyclisations of 3-Aroylchromones

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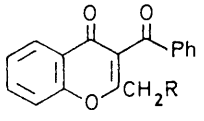
Whereas 3-benzoyl-2-methylchromone (1; R = H) does not undergo photocyclisation, its isomer, 3-(*o*-toluoyl)-chromone (2) produces a benzoxanthenone with ease; this implies that the electronic effects on the behaviour of the photochemical intermediates are delicately balanced. 2-Methyl-3-(*o*-toluoyl)chromone (5; R = H) also produces a benzoxanthenone on irradiation. Exploration of this last reaction with labelled substrates indicated that initial photoenolisation was followed by a rapid [1,7] sigmatropic hydrogen shift before cyclisation. Substituent effects on the process of photoenolisation are considered. The behaviour of the above chromones with base has been studied briefly.

As part of a general study of the scope of the photoenolisation reaction in synthetic work, the behaviour of some substituted chromones has been examined. Much work in this area has been described, principally by Ullman and his co-workers,[2-5] but certain of these results remain unexplained. For example,[2] whereas 3-benzoyl-2-methylchromone (1; R = H) did not appear to undergo photoenolisation, 2-benzyl-3-benzoylchromone (1; R = Ph) did so. It was not clear, however, whether this difference was merely due to a weakening of the carbon–hydrogen bond on the 2-substituent in the latter case, or to a lowering in energy of the initial excited state in the photoenolisation reaction. Relatively little is



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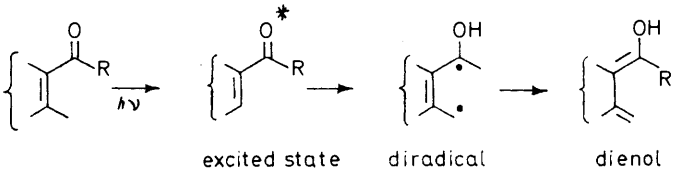
known about substituent effects in photochemical reactions. In the present work several chromones have been studied in order to explore general trends in the effect of alkyl substituents on photoenolisation and to extend the usefulness of the reaction for synthetic purposes.[6]

Previous studies have shown that formation of dienols is best demonstrated, in a chemical sense, by reaction with a dienophile. Use of oxygen as trapping agent may give ambiguous results, since it can react with either the dienol species (Scheme 1)[1,7-9] or, probably,



SCHEME 1

the precursor diradical.[8,10,11] Deuterium incorporation studies are only effective where the dienol species can revert to the starting carbonyl compound by a ground-state process, and this is not always the case.[10,12] In our hands, irradiation of the chromone (1; R = H) in benzene with a medium-pressure mercury lamp and in the presence of dimethyl butynedioate gave no adduct, even after extended periods. This result is consistent with the findings of Ullman *et al.*[2] that no deuterium exchange into the methyl group occurred when compound (1; R = H) was irradiated in the presence of deuteriomethanol. This chromone was also stable when irradiated in the presence of oxygen, implying that a diradical intermediate (see Scheme 1) is not formed. In this case, therefore, any excited states

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[1] Part IV, B. J. Arnold, P. G. Sammes, and T. W. Wallace, *J.C.S. Perkin I*, 1974, 415.

[2] K. R. Huffman, M. Loy, and E. F. Ullman, *J. Amer. Chem. Soc.*, 1965, **87**, 5417.

[3] W. A. Henderson, jun., and E. F. Ullman, *J. Amer. Chem. Soc.*, 1965, **87**, 5424.

[4] K. R. Huffman, M. Loy, W. A. Henderson, jun., and E. F. Ullman, *Tetrahedron Letters*, 1967, 931.

[5] K. R. Huffman, M. Loy, W. A. Henderson, jun., and E. F. Ullman, *J. Org. Chem.*, 1968, **33**, 3469.

[6] *Cf.* B. J. Arnold, S. M. Mellows, and P. G. Sammes, *J C.S. Perkin I*, 1973, 1266.

[7] G. Porter and M. F. Tchir, *J. Chem. Soc.* (*A*), 1971, 3772.

[8] P. Yates, A. C. Mackay, and F. X. Garneau, *Tetrahedron Letters*, 1968, 5389.

[9] T. Matsuura and Y. Kitaura, *Tetrahedron*, 1969, **25**, 4487.

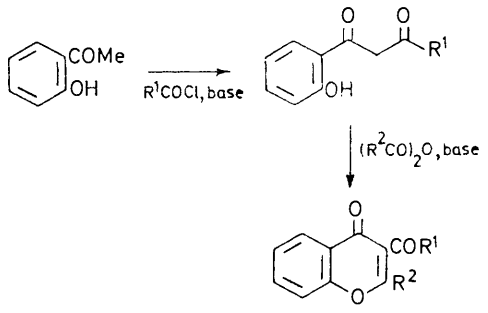
[10] B. J. Arnold, S. M. Mellows, P. G. Sammes, and T. W. Wallace, *J.C.S. Perkin I*, 1974, 401.

[11] J. Grotewold, C. M. Previtali, D. Soria, and J. C. Scaiano, *J.C.S. Chem. Comm.*, 1973, 207.

[12] G. Wettermark, *Photochem. and Photobiol.*, 1965, **4**, 621.

produced do not undergo reactions involving the methyl group but collapse to the ground state by alternative processes such as internal conversion.

The isomer (2) of the chromone (1; R = H), prepared by the route shown in Scheme 2, contains a system more

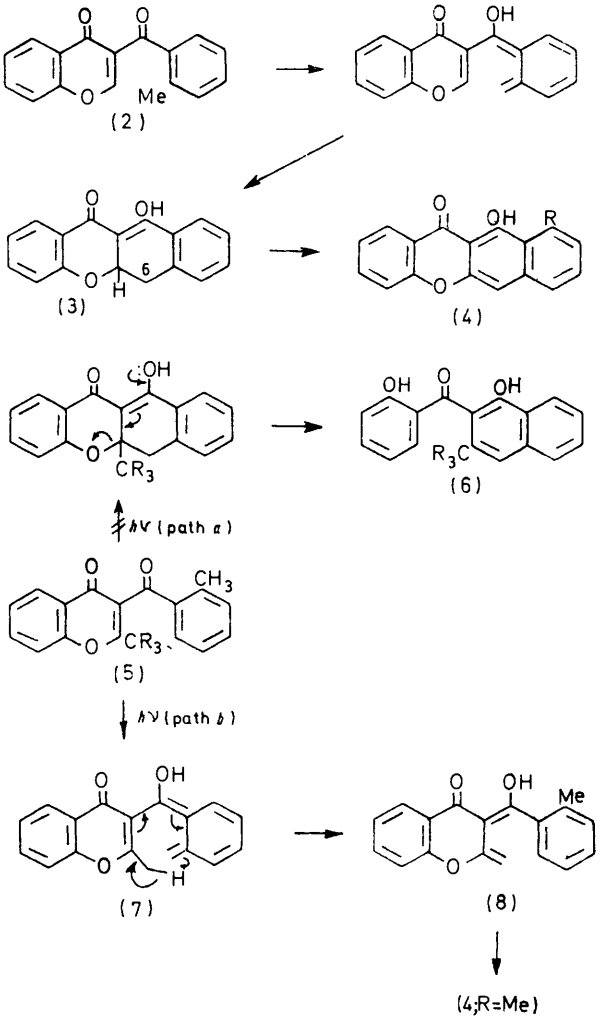


SCHEME 2

akin to a 2-methylbenzophenone, for which formation of photoenols is well documented.[13] When irradiated under the same conditions as (1; R = H) a smooth transformation of the chromone (2) occurred and the known benzoxanthenone (4; R = H) was isolated in 80% yield. Presumably photoenolisation does occur in this instance and is followed by a rapid cyclisation (hexatriene-to-cyclohexadiene type, either thermal or photochemical), which is aided by re-formation of the disubstituted benzene ring. The dihydrobenzoxanthenone (3), initially formed, undergoes rapid loss of hydrogen to give the fully aromatic system, a process which is common in these cyclisation reactions.[3] That the cyclisation process is rapid was demonstrated by the failure to trap the intermediate dienol with dimethyl butynedioate, the benzoxanthenone (4; R = H) again being formed in high yield.

An attempt was made to block the oxidation of the intermediate dihydro-species, of type (3), by inclusion of a methyl group in position 2, as in the chromone (5; R = H). It was hoped that this derivative would have the advantage of an alternative reaction pathway (Scheme 3, path *a*), which would lead to the naphthol (6; R = H), of novel substitution pattern and which would be of use as an entry into the substituted naphthacenes. In the event, photolysis of the chromone (5; R = H) proceeded smoothly to produce, not the naphthol (6), but the substituted benzoxanthenone (4; R = Me), identified on the basis of spectral comparison with the benzoxanthenone (4; R = H). This result suggested initially that the 2-methyl group had reacted, a behaviour incompatible with that of compound (1; R = H). In order to rationalise the distinct differences in photolability between the chromones (1; R = H) and (5; R = H), reaction path *b* in Scheme 3 was postulated. Direct participation of the 2-methyl group in photoenolisation of the disubstituted chromone (5; R = H) can be dismissed, since the presence of the second methyl group on the benzoyl substituent has little effect on its u.v. spectrum in comparison with that of the photostable system (1; R = H); nor should its presence introduce any dominant steric effects that might interfere with the (lack of) photochemical modification of the 2-methyl group. The postulated scheme requires a [1,7] hydrogen migration and this was demonstrated by means of an isotopic labelling experiment.

The deuterium-labelled chromone (5; R = ^{2}H) was prepared by using [$^2H_6$]acetic anhydride and sodium [$^2H_3$]acetate for the final condensation step (*cf.* Scheme 2). The ^{1}H n.m.r. and mass spectra of the product indicated a specific and high incorporation of deuterium into the 2-methyl group (>95% $^2H_3$). Irradiation of the labelled chromone (5; R = ^{2}H) gave the labelled benzoxanthenone (9). An n.m.r. assay, backed up by mass spectroscopic analysis, showed that the product

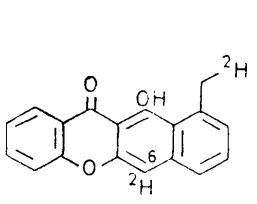


SCHEME 3

contained essentially one atom of deuterium in the methyl group and one atom at position 6, as expected for the participation of a [1,7] sigmatropic rearrangement; the other atom of deuterium was lost during aromatisation of the dihydro-intermediate. Some start-

[13] N. C. Yang and C. Rivas, *J. Amer. Chem. Soc.*, 1961, **83**, 2213.

ing material was also recovered and spectral analysis of this showed that some scrambling of the label had occurred between the methyl groups. Thus, although



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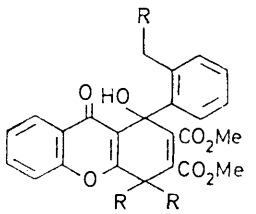

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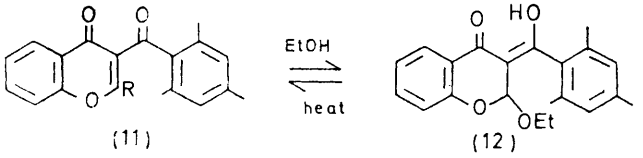
cyclisation to give the benzoxanthenone is the major reaction pathway, it cannot be completely efficient and some collapse of the dienol (8) must also occur by other reaction paths, which eventually re-form the starting material. These could include a photocatalysed reaction; such back reactions were noted by Ullman.[2]

The operation of the sigmatropic rearrangement appears to follow rapidly upon formation of the initial dienol (7). Addition of dimethyl butynedioate to the (unlabelled) chromone (5; R = H) during irradiation did not trap the initial dienol (7) but rather the final dienol (8), to form the dihydroxanthone (10; R = H). The identity of the adduct was readily deduced by repeating the reaction with the labelled chromone (5; R = ^{2}H). In this case the labelled product (10; R = ^{2}H) gave the expected ^{1}H n.m.r. spectrum.

The above result suggests that, whereas the chromone (1; R = H) does not photoenolise, the corresponding



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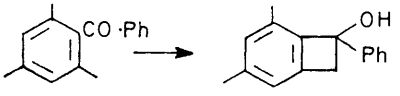


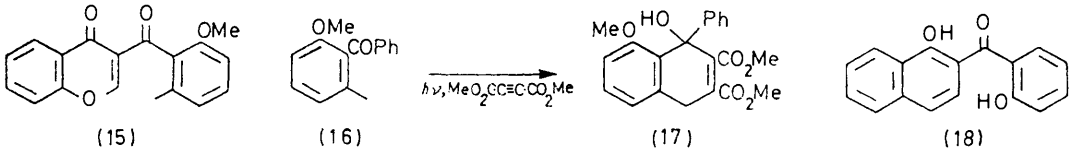
(13) (14)

ground-state dienol should be capable of existence, as exemplified by trapping of the dienol (8). The photochemical reaction must be blocked at an earlier stage in the photoenolisation process (Scheme 1) and this suggests either that the diradical has a higher energy level than the excited state or that the latter has available a more rapid path for its decay into the ground state than *via* formation of the diradical.

The mesitoyl derivative (11; R = H) was also examined. When recrystallised from ethanolic solutions, this compound readily added ethanol to form the adduct (12), but the starting material could be regenerated by heating under reduced pressure. This chromone was of interest for comparison with the corresponding mesitophenone system (13), which is known to behave anomalously during irradiation. In the case of this ketone, which bears two *ortho*-substituents, photochemical reaction does not appear to produce the ground-state dienol, instead the benzocyclobutenol (14) is formed. Although heating the product alcohol regenerates the ketone,[14] heating it in the presence of dimethyl butynedioate does not give an adduct. Furthermore, attempts to introduce deuterium by an exchange process also failed during irradiation of this ketone.[9] These results imply that hydrogen abstraction to form the diradical intermediate can occur with this ketone, but that initial collapse to the dienol is inhibited, probably by steric effects. When the chromone (11; R = H) was irradiated, either in the absence or in the presence of dimethyl butynedioate, no new photochemical products were observed. The same was true of the methyl analogue (11; R = Me). Even prolonged irradiation of the deuteriated analogue [11; R = C(^{2}H)$_3$] gave no observable scrambling of the deuterium label. The absence of any benzocyclobutenol was unexpected and again suggests a delicate balance between the various excited states and their dependence, in this case, on both substituent effects and conformational restrictions imposed by the hindered rotation about the aroyl-chromone links. Adoption of the correct conformational forms is probably critical for the partition of the excited state energy between the various decay paths.

In the expectation that the presence of a methoxy-group *ortho* to the carbonyl function would stabilise the corresponding dienol by hydrogen bonding, the chromone (15) was prepared. Initial experiments with the corresponding benzophenone (16) (two *ortho*-substituents) indicated that photoenolisation was possible, in contrast to the mesitoyl series, and that trapping with dimethyl butynedioate did give the expected adduct (17) in good yield. In contrast, the chromone (15) did not undergo the expected photocyclisation, a result which can only be explained by an adverse combination of electronic and steric effects.

To summarise, photoenolisation appears to be very dependent on steric [9,14] as well as electronic factors The former can control whether or not initial hydrogen abstraction is spatially possible and whether the diradical thus formed is able to collapse into the ground-state dienol. Electronic effects are dominant in determining the type and level of the excited states involved



(15) (16) (17) (18)

[14] Y. Kitaura and T. Matsuura, *Tetrahedron*, 1971, **27**, 1597.

in the process. For complex molecules, the type of electronic excitation involved (predominant n–π^* or π–π^* types) may not be as important as was originally anticipated from studies with simpler models. Hydrogen abstraction by π–π^* excited states has precedent,[15,16] although formation of a ground-state dienol by such a process has not yet been categorically demonstrated.[17] As pointed out above, the partition of excited-state energy in complex molecules, such as the aroylchromones, must also depend on the conformational relationship amongst the various functional groups.

A different approach to the cyclisation reactions described above has also been pursued. Dienolate anions should behave in a manner similar to dienols and, since nucleophilic addition–elimination reactions across chromones are well exemplified,[18] a base-induced cyclisation of the chromone (2) was attempted. Treatment with lithium di-isopropylamide in tetrahydrofuran produced a deep red anion, which underwent the desired reaction to form the substituted naphthol (18), although only in moderate yield. The latter reaction is similar in concept to the novel route to anthraquinones described by Hassall and his co-workers.[19,20] Similar treatment of the chromones (1; R = H) and (5; R = H) was abortive.

EXPERIMENTAL

General experimental details were as described previously.[10] T.l.c. on silica gel GF_{254} (Merck) was used to follow reactions; preparative t.l.c. was carried out using 1 mm thick plates of the same stationary phase. Compositions of mixtures of solvents, which were dried before use, are quoted as ratios by volume. Extracts were dried with anhydrous sodium sulphate and evaporated under reduced pressure. Photolyses were carried out in Pyrex vessels, or, if stated, quartz flasks, fitted with glass sinters. Unless otherwise specified, solutions were irradiated under dry nitrogen and were initially purged with the gas for at least 20 min. The light source was a 450 W medium-pressure mercury vapour lamp, emitting a broad spectrum with peak output near 366 nm.

For compounds marked with an asterisk, spectral data are available as Supplementary Publication No. SUP 21431 (10 pp., 1 microfiche).†

3-(o-*Toluoyl*)*chromone* (2).—1-(2-Hydroxyphenyl)-3-(*o*-tolyl)propane-1,3-dione [21] (m.p. 97—98°; 1.07 g), sodium formate (1.1 g), and acetic formic anhydride (8 ml) were stirred at room temperature for 24 h. Water (10 ml) was added and the mixture extracted with chloroform (3 × 30 ml). The extracts were washed with aqueous sodium carbonate (10%; 2 × 30 ml) and water (30 ml), dried and evaporated to give the title *compound* * as a solid. Recrystallisation from ethanol gave needles, m.p. 161—163° (Found: C, 77.1; H, 4.7. $C_{17}H_{12}O_3$ requires C, 77.3; H, 4.6%).

† For details of Supplementary Publications see Notice to Authors No. 7, *J.C.S. Perkin I*, 1974, Index issue.

[15] N. J. Turro, 'Molecular Photochemistry,' Benjamin, New York, 1965, p. 152.
[16] A. G. Schultz, C. D. DeBoer, W. G. Herkstroeter, and R. H. Schlessinger, *J. Amer. Chem. Soc.*, 1970, **92**, 6086.
[17] But see A. C. Pratt, *J.C.S. Chem. Comm.*, 1974, 183.
[18] S. Wawzonek, 'Heterocyclic Compounds,' ed. R. C. Elderfield, Wiley, New York, 1950, vol. 2, p. 229.

2-*Methyl*-3-(o-*toluoyl*)*chromone* (5; R = H).—This was prepared in a manner similar to compound (2), with acetic anhydride in place of acetic formic anhydride and fused sodium acetate in place of sodium formate. The reaction was conducted at 110 °C for 30 min, the mixture was poured onto ice and the solid product was filtered off, washed with water and dissolved in chloroform. The solution was washed with aqueous sodium hydrogen carbonate, dried, and evaporated to give the *chromone* * (95%), which crystallised from ethanol as needles, m.p. 134—135° (Found: C, 77.6; H, 5.2. $C_{18}H_{14}O_3$ requires C, 77.7; H, 5.1%).

2-([$^2H_3$]*Methyl*)-3-(o-*toluoyl*)*chromone* * (5; R = ^{2}H) was prepared in a completely analogous way, with sodium [$^2H_3$]acetate and [$^2H_6$]acetic anhydride in place of the unlabelled substrates. A mixed m.p. with the unlabelled compound showed no depression.

3-*Mesitoylchromone* (11; R = H).—*o*-Hydroxy-2-mesitoylacetophenone [22] (0.6 g), sodium formate (0.7 g), and acetic formic anhydride (3 ml) were stirred at room temperature for 24 h. Water (8 ml) was added and the solution extracted with chloroform (2 × 20 ml). The extract was washed with water and dried. Evaporation and crystallisation from ethanol gave the *solvate* * (12), m.p. 100° (decomp.) (Found: C, 74.7; H, 6.9. $C_{21}H_{22}O_3$ requires C, 74.5; H, 6.55%).

Heating the solvate under reduced pressure at 150 °C for 2 h and crystallising the product from acetone–hexane gave the *chromone* * (11; R = H) (overall yield 54%), m.p. 137—139° (Found: C, 78.1; H, 5.6. $C_{19}H_{16}O_3$ requires C, 78.1; H, 5.5%).

2-*Methyl*-3-*mesitoylchromone* (11; R = Me).—By using the standard conditions this *chromone* * was obtained in 74% yield. Recrystallised from ethanol this did not form a solvate, and had m.p. 156—158° (Found: C, 78.6; H, 6.1. $C_{20}H_{18}O_3$ requires C, 78.4; H, 5.9%).

This preparation was repeated with sodium [$^2H_3$]acetate and [$^2H_6$]acetic anhydride in place of the unlabelled reagents, to produce the labelled *chromone* * [11; R = $C(^2H)_3$], m.p. not depressed on mixing with the unlabelled substance.

2-*Methoxy*-6-*methylbenzophenone* (16).—2-Methoxy-6-methylbenzoyl chloride [23] (3.0 g) in benzene (50 ml) was treated with powdered aluminium chloride (6.0 g) at 0 °C for 1 h. The mixture was then heated to reflux for a further 1.5 h, cooled, poured onto ice–water, and extracted with ether (3×). The organic phase was washed with aqueous sodium carbonate, dried, treated with charcoal, and evaporated. The residual oil, mainly the 2-hydroxy-derivative, was re-methylated with dimethyl sulphate under standard conditions to give the title *compound* * (3.4 g, 95%), b.p. 200° at 10 mmHg, m.p. 60—65° (Found: C, 79.7; H, 6.3. $C_{15}H_{14}O_2$ requires C, 79.6; H, 6.2%).

3-(2-*Methoxy*-6-*methylbenzoyl*)*chromone* (15).—*o*-Hydroxyacetophenone (1.13 g) in pyridine (5 ml) containing 2-methoxy-6-methylbenzoyl chloride (1.56 g) was stirred at room temperature for 2 h. The mixture was poured into 2N-hydrochloric acid (100 ml) and extracted with ether. The pale yellow oil obtained after isolation was not charac-

[19] J. S. Davies, V. H. Davies, and C. H. Hassall, *J. Chem. Soc.* (*C*), 1969, 1873.
[20] C. H. Hassall and B. A. Morgan, *J.C.S. Perkin I*, 1973, 2853.
[21] F. Cramer and G. H. Elschnig, *Chem. Ber.*, 1956, **89**, 1.
[22] C. T. Davis and T. A. Geissman, *J. Amer. Chem. Soc.*, 1954, **76**, 3507.
[23] S. E. Cremer and D. S. Tarbell, *J. Org. Chem.*, 1961, **26**, 3653.

terised but was immediately dissolved in ethyl formate (30 ml) in which sodium (375 mg) had been dissolved. The mixture was stirred at room temperature for 12 h before addition to ice (40 g) and 2N-hydrochloric acid (100 ml). The mixture was stirred for 1 h before extraction with chloroform. After drying, the extract was evaporated to give a brown oil. This was dissolved in ethyl acetate and treated with charcoal, before filtration through Celite and evaporation, to give yellow needles of 1-(2-*hydroxyphenyl*)-3-(2-*methoxy*-6-*methylphenyl*)*propane*-1,3-*dione* * (0.96 g, 41%), m.p. 104—106° (Found: C, 71.8; H, 5.8. $C_{17}H_{16}O_4$ requires C, 71.8; H, 5.7%).

The phenol (466 mg), sodium formate (535 mg), and acetic formic anhydride (8 ml) were stirred at room temperature for 24 h. Water (10 ml) was added and the product extracted with chloroform (3 × 25 ml). The organic phase was dried and evaporated to yield needles of 3-(2-*methoxy*-6-*methylbenzoyl*)*chromone* * (15) (272 mg, 56%), m.p. 140—141° (from acetone–hexane) (Found: C, 73.45; H, 5.1. $C_{18}H_{14}O_4$ requires C, 73.4; H, 4.8%).

Irradiation of 3-*Benzoyl*-2-*methylchromone*.[24]—The chromone (1; R = H) (85 mg) in benzene (50 ml) was irradiated with the 450 W source through Pyrex under dry nitrogen in the presence of dimethyl butynedioate (310 mg). No reaction was observed after 12 h. No reaction was again observed when the experiment was repeated under oxygen in the absence of the ester.

Irradiation of the Chromone (2).—The chromone (25 mg) in benzene (40 ml) was irradiated with the 450 W source for 12 h. The solution was evaporated and the product subjected to preparative t.l.c. with chloroform as eluant. The main, non-polar product was 11-hydroxybenzo[*b*]-xanthen-12-one (4; R = H) (20 mg, 80%), m.p. 205—209° (from hexane–chloroform) (lit.,[3] 198—203°).

With dimethyl butynedioate (136 mg) the chromone (43 mg) (molar ratio 6 : 1, respectively) again gave only the benzoxanthenone, after irradiation for 12 h with the 450 W lamp.

Irradiation of the Chromone (5; R = H).—The chromone (90 mg) was irradiated in benzene (40 ml) with the 450 W source for 10 h. The solution was evaporated and the residue triturated with ether to give 10-*methyl*-11-*hydroxybenzo*[b]*xanthen*-12-*one* * (4; R = Me) (52 mg, 58%), m.p. 207—210° (from ethanol) (Found: C, 78.1; H, 4.6. $C_{18}H_{12}O_3$ requires C, 78.25; H, 4.4%).

The deuteriated chromone (5; R = ^{2}H) (109 mg) was irradiated under similar conditions for 10 h. Examination of a sample by ^{1}H n.m.r. spectroscopy showed that only chromone and benzoxanthenone were present (ratio 3 : 7). The combined product mixture was shaken with water and evaporated; the benzoxanthenone * (9) then crystallised out as orange needles (34 mg, 32%). The residue from the reaction mixture was separated by preparative t.l.c. to recover the chromone *.

Preparation of the Xanthone (10; R = H).—The chromone (5; R = H) (88 mg) and dimethyl butynedioate (220 mg, 5 equiv.) in benzene (40 ml) were irradiated for 12 h with the 450 W source. ^{1}H N.m.r. analysis indicated the starting chromone, benzoxanthenone, and an adduct to be present in the ratio 2 : 3 : 4. Isolation, by preparative t.l.c., afforded *dimethyl* 1,4-*dihydro*-1-*hydroxy*-10-*oxo*-1-*o*-*tolylxanthen*-2,3-*dicarboxylate* (30 mg), m.p. 165—195° (decomp.) (from hexane–chloroform) (Found: C, 68.3; H, 4.8. $C_{24}H_{20}O_7$ requires C, 68.6; H, 4.8%).

The labelled chromone (5; R = ^{2}H) (80 mg) and dimethyl butynedioate (182 mg) similarly gave the xanthone * (10; R = ^{2}H).

Irradiation of the Chromones (11).—The chromone (11; R = H) (28 mg) in benzene (45 ml) was unaffected by exposure to the 450 W lamp for 12 h. A similar result was obtained for the methylated derivative (11; R = Me), both in the absence and in the presence of dimethyl butynedioate.

The deuteriated analogue [11; R = C(^{2}H)$_3$] was irradiated, in benzene solution, in both Pyrex and quartz apparatus. In neither case did ^{1}H n.m.r. analysis indicate any scrambling of the labelled atoms, even after long irradiation times (Pyrex apparatus 56 h).

Irradiation of 2-*Methoxy*-6-*methylbenzophenone* (16).—The ketone (159 mg) and dimethyl butynedioate (190 mg) in benzene (45 ml) were irradiated with the 450 W source for 8 h. Evaporation afforded *dimethyl* 1,4-*dihydro*-1-*hydroxy*-8-*methoxy*-1-*phenylnaphthalene*-2,3-*dicarboxylate* (17) (180 mg, 70%) as needles, m.p. 135—169° (decomp.) (Found: C, 68.3; H, 5.65. $C_{21}H_{20}O_6$ requires C, 68.5; H, 5.5%).

Irradiation of the Chromone (15).—The chromone (58 mg) in benzene (45 ml) was irradiated through Pyrex with the 450 W lamp for 10 h, after which no reaction could be detected.

Treatment of the Chromone (2) *with Base*.—To a stirred solution of di-isopropylamine (428 mg) in tetrahydrofuran (5 ml) under nitrogen at −5 °C was added a solution of n-butyl-lithium in hexane (2.1M; 2 ml). After 15 min the chromone (2) (101 mg) in tetrahydrofuran (8 ml) and hexamethylphosphoric triamide (2 ml) was added over 10 min. After 2 h at −5 °C the mixture was warmed to 25 °C and left for a further 22 h. N-Sulphuric acid (35 ml) was added and the products were extracted with ether (2 × 60 ml). The extract was washed with water, dried, and evaporated and the residue was separated by preparative t.l.c. (2 : 3 chloroform–hexane as eluant). The non-polar, yellow material was extracted and crystallised from hexane to give 2-(2-*hydroxybenzoyl*)-1-*naphthol* * (18) (24.5 mg, 24%), m.p. 111—113° (Found: C, 77.2; H, 4.55. $C_{17}H_{12}O_3$ requires C, 77.3; H, 4.6%).

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