

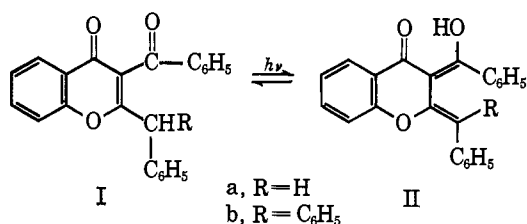
Photochemistry of 2-Benzyl- and 2-Benzhydryl-3-benzoylchromones

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The principal photochemical reaction of the title compounds Ia and Ib in benzene is photoenolization to give IIa and IIb. The reaction has been found to proceed exclusively via the triplet state. In ethanol and isopropyl alcohol a reaction related to photopinacolization is also observed, and the same triplet intermediate is again implicated. The rate of enolization relative to hydrogen abstraction from solvent by the chromone Ia triplet is compared to that of *o*-alkylbenzophenones. The photoenols IIa and IIb undergo photocyclization reactions in which singlet intermediates are demonstrated. By contrast, the enols undergo light-induced reketonization on excitation to their triplets. The evidence demands that intersystem crossing of singlet enol IIa, which has a strong intramolecular hydrogen bond, occurs very inefficiently or not at all. It is suggested that similar inefficient crossing of the singlets of the internally hydrogen-bonded *o*-hydroxyphenyl ketones may account for the exceptional photostability of these compounds.

Irradiation of solutions of 2-benzyl- or 2-benzhydryl-3-benzoylchromones (Ia and Ib) with ultraviolet light has been shown to produce orange colors which fade spontaneously in the dark.¹ The colored species have been assigned the corresponding enol structures IIa and IIb, and evidence has been presented that the fading process leads to the reformation of I, at least in the presence of alcohol.¹ However, even after fading ceases, these solutions frequently retain a residual pale yellow color, which suggests the occurrence of some irreversible photochemical process. Since the nature of this process might provide further insight into the



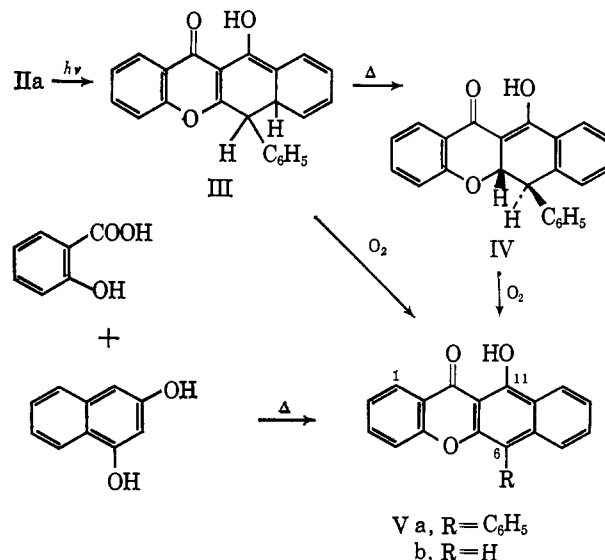
mechanism of the photoenolization process, a study was made of the photodegradation reactions of the two chromones.

Photochemistry of 2-Benzyl-3-benzoylchromone (Ia). Upon brief irradiation (1–2 min.) of solutions of Ia with ultraviolet light, the orange photoenol IIa was formed. While this species had only a few seconds of lifetime in alcohol, and thus could not readily be studied spectroscopically, in degassed benzene solution it displayed a single absorption maximum in the visible spectrum at 460 m μ which faded very slowly by approximately first-order kinetics ($k_{25^\circ} \approx 2 \times 10^{-5}$

(1) K. R. Huffman, M. Loy, and E. F. Ullman, *J. Am. Chem. Soc.*, 87, 5417 (1965).

sec.⁻¹). On longer irradiation in degassed benzene the visible absorption band became very intense and slowly shifted to shorter wave length. After the maximum had reached 400 m μ no further change occurred either on longer irradiation or on standing in the dark. This same 400-m μ absorption also appeared upon irradiation of a solution containing the enol IIa with light of sufficiently long wave length (>430 m μ) that it was absorbed by the enol but not by the starting chromone Ia. On admission of oxygen to the solution containing the 400-m μ compound, this peak rapidly disappeared with the formation of a new absorption maximum at 440 m μ .

It was found possible to prepare the compound absorbing at 440 m μ in high yield (71%) by simultaneous irradiation of a benzene solution of Ia with a very intense visible light (>430 m μ) together with somewhat weaker ultraviolet radiation (310–390 m μ) while bubbling in oxygen. This product Va was related to Ia by the loss of two hydrogen atoms and displayed no aliphatic hydrogen signals in its n.m.r. spectrum. Comparison of Va with 11-hydroxy-12H-benzo[*b*]xanthen-12-one (Vb), prepared by heat-induced condensation of salicylic acid with 1,3-naphthalenediol, revealed close similarities. Both compounds were weakly acidic, gave positive ferric chloride tests, and had very similar electronic absorption spectra (see Figure 1). Both displayed weak, broad peaks in the infrared at 3.70 μ (CHCl₃), characteristic of a strongly hydrogen-bonded hydroxyl, and nearly identical carbonyl peaks (6.15 and 6.12 μ for Va and Vb, respectively).



These data establish with reasonable certainty the existence of an 11(or 1)-hydroxy-12H-benzo[*b*]xanthen-12-one nucleus in Va but leave in doubt the position of the phenyl residue. The location of this residue in Va

at the 6-position and *para* to the hydroxyl is based on two arguments. First, of the five 12H-benzo[*b*]xanthen-12-ones, Va, Vb, VIIa, VIIb, and VIIa, prepared in this study, only those known to bear hydrogen at the 6-position, Vb and VIIa (*vide infra*), displayed a strong aromatic C-H bending peak in the infrared at 12.0 μ , and this peak was absent in the spectrum of Va. Second, Va failed to couple with benzenediazonium chloride or give a positive Gibbs test² (diagnostic of *para*-unsubstituted phenols) whereas the 6-unsubstituted 11-hydroxybenzo[*b*]xanthen-12-one Vb gave positive tests with both these reagents.

In order to identify the 400-m μ oxygen-sensitive precursor III of the benzoxanthenone Va, a benzene solution of III was produced by irradiation with ultraviolet and visible light exactly as Va had been prepared but in the absence of oxygen. However, even very careful evaporation of the solvent *in vacuo* produced spectral changes which suggested that a mixture of new products had been formed (see Experimental Section). On the other hand, when the solution was first boiled for 24 hr. and then evaporated *in vacuo*, a single somewhat more stable product IV could be isolated by careful crystallization of the residue from ethanol under nitrogen. Compound IV was isomeric with the starting chromone Ia. Although it had an absorption maximum in benzene at 400 m μ , identical with that of III, the two compounds were indeed different since the coincidence in position of the 400-m μ maxima was absent in other solvents.

Solutions of both the initially formed photoproduct III and its thermal reaction product IV were found to oxidize spontaneously in the air to give the benzoxanthenone Va, although IV oxidized much more slowly. Both compounds thus appeared to be dihydrobenzoxanthenones. Although addition of alkali to an alcoholic solution of III led to nearly instantaneous disappearance of the visible absorption band, the same conditions produced a shift in the visible absorption maximum of IV from 391 to 414 m μ and thus the presence of a weakly acidic grouping in this compound was indicated. This conclusion was supported by the reappearance of the original spectrum on acidification of basic solutions of IV. Judging from the infrared spectrum of IV, which had distinctive peaks at 6.18 (hydrogen-bonded ketone) and 3.33 μ (hydrogen-bonded hydroxyl), the acidic grouping was most likely an enolized β -diketone. While the n.m.r. spectrum of III could not be obtained, the n.m.r. spectrum of IV displayed a characteristic AB pattern with doublets ($J = 12.0$ c.p.s.) arising from proton resonances at τ 4.53 and 5.54 (CDCl₃). The higher field doublet showed additional very weak coupling which manifested itself as a slight broadening of the peaks. These data require two aliphatic vicinally related but otherwise nearly isolated *trans*-oriented protons, the more shielded of which probably is positioned to permit weak long range coupling with an olefinic proton. Thus, if it is accepted that the ring skeletons of IV and Va are the same, the only structure for the more stable 400-m μ product that will accommodate these data is that given for IV.

The initial highly unstable photochemically produced product III is then most probably a nonaromatic but

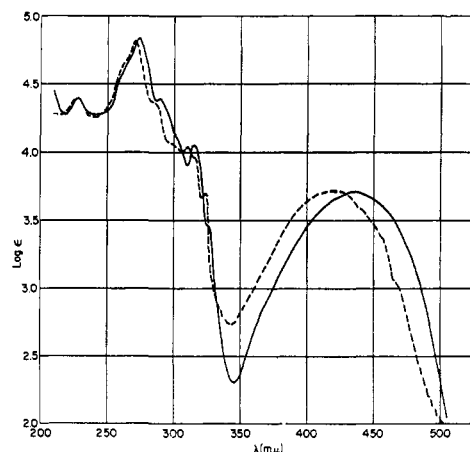
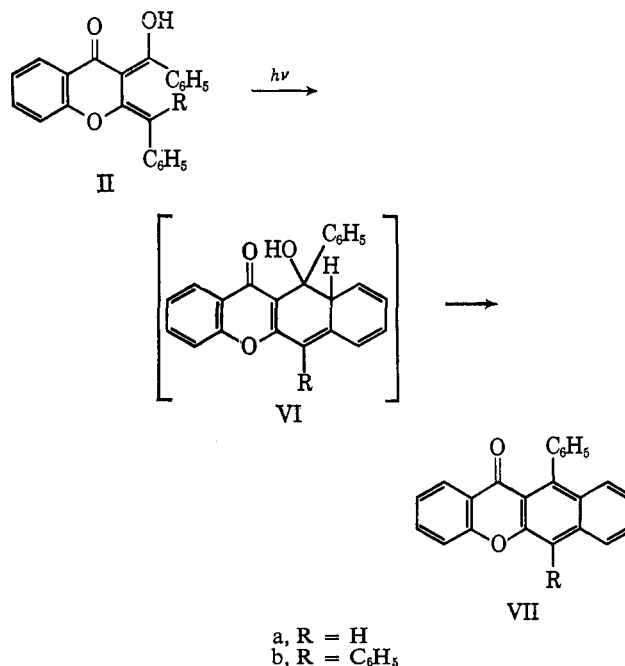


Figure 1. Absorption spectra of 11-hydroxy-6-phenyl-12H-benzo[*b*]xanthen-12-one (Va), —, and 11-hydroxy-12H-benzo[*b*]xanthen-12-one (Vb), - - - - - , in cyclohexane solution.

highly conjugated double bond isomer of IV. Since the appearance of its 400-m μ maximum during visible light irradiation of the enol IIa was concerted with the disappearance of the enol 460-m μ maximum (isosbestic points at 356 and 440 m μ), no long-lived intermediate is produced. The product III is therefore probably derived from IIa in a one-step process. The assigned structure for III, while not rigorously established, is the most plausible precursor for IV, and can indeed be derived from the photoenol IIa by a single-step photocyclization process that finds direct analogy in a related reaction of the photoenol of *o*-methylbenzophenone.³

In addition to the benzoxanthenone Va, two minor products were also isolated when the chromone Ia was exposed to both ultraviolet and visible light in the presence of oxygen. One of these, VIIa, obtained in 3.4% yield, was found to be related to the starting material



by the loss of the elements of water. From the very close similarity of the ultraviolet spectra (Figure 2)

(3) E. F. Ullman and K. R. Huffman, *Tetrahedron Letters*, 1863 (1965).

(2) H. D. Gibbs, *J. Biol. Chem.*, **72**, 649 (1927).

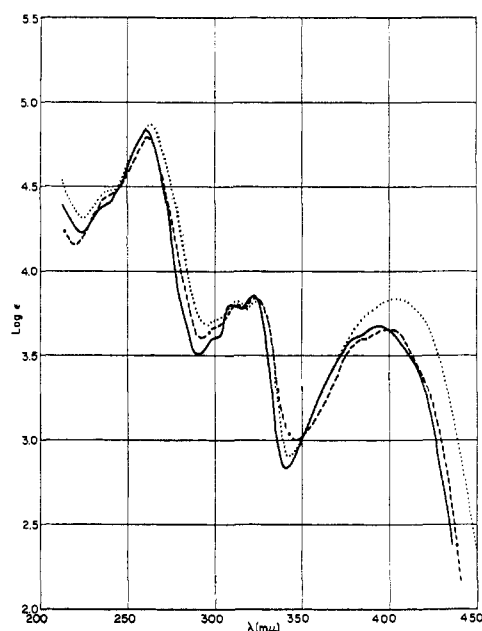
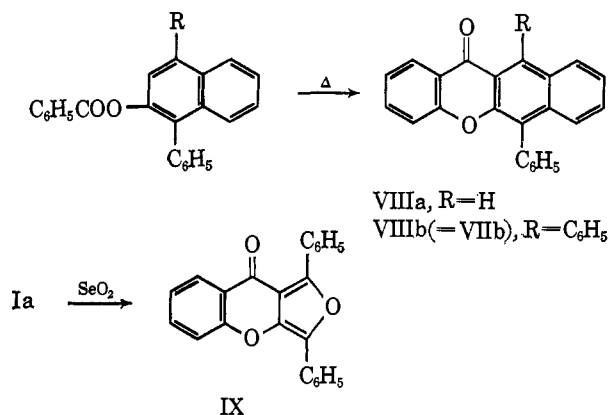


Figure 2. Absorption spectra of 11-phenyl-12H-benzo[b]xanthen-12-one (VIIa), ———, 6-phenyl-12H-benzo[b]xanthen-12-one (VIIIa), - - - - -, and 6,11-diphenyl-12H-benzo[b]xanthen-12-one (VIIIb), ······, in absolute ethanol solution.

of VIIa and of the model compounds 6-phenyl- and 6,11-diphenyl-12H-benzo[b]xanthen-12-ones (VIIIa and VIIIb, respectively, synthesized as shown below) and the identical infrared carbonyl absorption of all these compounds at 6.05μ , VIIa appears to be a phenyl-substituted 12H-benzo[b]xanthen-12-one. Since VIIa

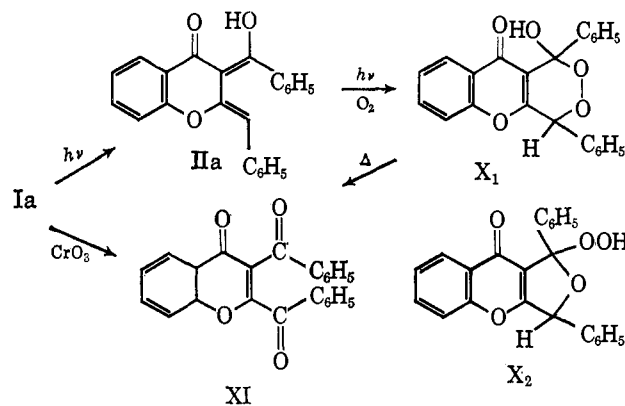


is different from the isomeric model VIIIa, the phenyl group cannot be in the 6-position. Thus, barring some unlikely very deep-seated rearrangement, VIIa probably has the phenyl substituent at the 11-position. A very plausible reaction sequence for the formation of this product by way of the hydrated intermediate VIa can then be written.

The other minor product, isolated in $<1\%$ yield, was bright yellow and displayed a single carbonyl peak in the infrared at 5.98μ and only aromatic hydrogen signals in the n.m.r. spectrum. Since it was identical with a dehydro derivative of Ia prepared by selenium dioxide oxidation of the chromone Ia, it was assigned the furan structure IX.

When the irradiation was carried out in the presence of oxygen but without the use of visible light, the yield of each of these products Va, VIIa, and IX was de-

creased and two new products were obtained. One of them, X, isolated in 13% yield by crystallization, had a composition corresponding to the addition of oxygen to IIa. Its spectra were typical of the chromone nucleus⁴ with peaks in the ultraviolet at 263 (sh), 296, and 303 m μ , and in the infrared at 6.10 (C=O), 6.38, 7.20, and 10.88 μ . Distinctive hydroxyl absorption in the infrared at 2.94 μ was also observed. The compound gave positive tests for peroxide with ferrous thiocyanate and with potassium iodide in hot acetic acid. It displayed signals in the n.m.r. spectrum corresponding to a hydroxyl hydrogen at τ 1.82 (disappears on addition of deuterium oxide) and a single aliphatic hydrogen at 3.47 (singlet). On heating X to its melting point or on dissolution in methanol, water was eliminated with a near-quantitative formation of the second product XI. This second product was also isolated in 40% yield directly from the reaction mixture by chromatography of the mother liquors remaining from the recrystallization of X. It no longer gave a nonaromatic proton signal in its n.m.r. spectrum, and it displayed a new maximum in the infrared at 5.95 μ attributable to an aromatic ketone. Synthesis of this compound by chromic anhydride oxidation of the chromone Ia provides strong evidence for structure XI, but leaves several possible structures for its precursor X. Of these only X₁ and X₂ need be seriously



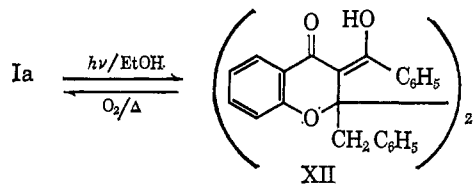
considered, since these are the only structures that do not require complex skeletal rearrangements. The cyclic peroxide structure X₁ is favored over the hydroperoxide X₂ because (1) reduction by potassium iodide occurred in boiling acetic acid, as is characteristic of dialkyl peroxides including photoadducts of 1,3-dienes with oxygen, and did not occur at an appreciable rate in boiling isopropyl alcohol containing a little acetic acid as would be expected if X were a hydroperoxide⁵; and (2) the product expected by analogy with the often observed photochemical addition of oxygen to dienes⁶ is the cyclic peroxide X₁.

(4) (a) For the ultraviolet spectra of some related chromones see D. Pillon, *Bull. soc. chim. France*, [5] 19, 324 (1952), and B. K. Ganguly and P. Bagchi, *J. Org. Chem.*, 21, 1415 (1956); (b) among 16 chromones described in this and the preceding paper,¹ the carbonyl infrared maxima (mull or CHCl₃) were all in the range 6.07–6.14 μ , and three additional strong peaks were also always present at 6.33–6.38, 7.10–7.30, and 10.28–10.80 μ .

(5) (a) F. H. Dickey, F. F. Rust, and W. E. Vaughan, *J. Am. Chem. Soc.*, 71, 1432 (1949); (b) C. D. Wagner, R. H. Smith, and E. D. Peters, *Anal. Chem.*, 19, 976 (1947).

(6) For leading references see (a) G. O. Schenck and E. Koch, *Z. Elektrochem.*, 64, 170 (1960); (b) E. J. Bowen in "Advances in Photochemistry," Vol. 1, W. A. Noyes, G. S. Hammond, and J. N. Pitts, Jr., Ed., Interscience Publishers, Inc., New York, N. Y., 1963, p. 23; (c) C. S. Foote and S. Wexler, *J. Am. Chem. Soc.*, 86, 3879, 3880 (1964).

When ethanol instead of benzene was used as solvent, irradiation of an oxygen-free solution of the chromone Ia with ultraviolet light produced less than 1% of the benzoxanthenones Va and VIIa. Instead, there precipitated from the reaction mixture in 51% yield a new product XII, which by combustion analysis appeared to be related to the starting chromone Ia by the addition of 1-3 hydrogen atoms per chromone molecule, but which had roughly double the molecular weight. This product lacked the characteristic chromone ultraviolet and infrared absorption⁴ but displayed infrared maxima at 6.18 (C=O) and 3.42 μ (OH), consistent with the absorption expected by a hydrogen-bonded enolized β -diketone. The presence of a singlet at τ 0.38 in the n.m.r. spectrum likewise suggested the presence of a hydrogen-bonded hydroxyl grouping. In



addition, the spectrum showed an AB quartet arising from proton resonances at τ 5.49 and 5.89 (C_6D_6), with twice the area of the hydroxyl signal. The high coupling constant ($J = 16.0$ c.p.s.) of the quartet provided strong evidence for a methylene group bearing hydrogens in different magnetic environments, as expected if the methylene were attached to an asymmetric carbon atom.

When this product was heated for 5 min. at its melting point in air, oxygen was consumed and water was formed as shown by mass spectrometry. The organic product, which was formed in excess of 1 equiv., was the starting chromone Ia. The photoproduct must then be a reduction dimer of the chromone, and from the spectral data, it must have a structure corresponding to one of the two possible stereoisomeric forms of XII.

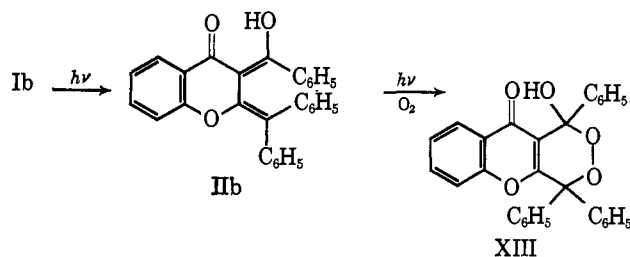
When the irradiation was carried out using isopropyl instead of ethyl alcohol as solvent, the same product XII was formed. However, when using poorer hydrogen donors such as methanol or toluene as solvents, no reduction dimer was produced.

Photochemistry of 2-Benzhydryl-3-benzoylchromone (Ib). The photochemical reactions of Ib were with one exception qualitatively parallel to those of the benzylchromone Ia. The photoenol IIb, λ_{max} 449 $m\mu$, generated by brief irradiation of a degassed benzene solution of Ib, did not fade at an observable rate in this solvent although it did fade on addition of a hydroxylic solvent. Irradiation of the enol IIb with light not absorbed by the chromone Ib (>430 $m\mu$) caused a drop in the 449- $m\mu$ peak with the appearance of new maxima at 392 and 408 $m\mu$. However, the spectral changes involved no isosbestic points and suggested that a dark reaction proceeding at a rate similar to the photochemical process was involved in the formation of the new species. The compound responsible for these new visible absorption maxima could be isolated in 76% yield after prolonged ultraviolet irradiation. This product was related to the starting chromone Ib by the loss of 1 mole of water, and proved by direct comparison to be identical with the diphenylbenzoxanthenone VIIIb described above. Thus, the thermally

unstable intermediate formed during the irradiation is probably the hydroxychromone VIb. The reaction finds complete analogy in the formation of the minor product VIIa from the benzylchromone Ia.

In addition to VIIIb the reaction mixture afforded a small amount (1.6%) of the 6-phenylbenzoxanthenone VIIIa which likewise was identified by comparison with an authentic sample. The analogous product, the unsubstituted 12H-benzo[*b*]-xanthen-12-one, was not observed on irradiation of the benzylchromone Ia.

Irradiation of the benzhydrylchromone Ib with ultraviolet light in the presence of oxygen gave, in addition to 40% of the diphenylbenzoxanthenone VIIIb, 21% of an oxygen adduct XIII. Like the peroxide X, this compound displayed ultraviolet and infrared absorption typical of the chromone nucleus as well as hydroxyl absorption at 3.02 μ . The compound also appeared to be a cyclic peroxide rather than a hydroperoxide since it was reduced by potassium iodide in boiling acetic acid but not in boiling isopropyl alcohol. The assigned structure, like X, depends on the assumption of no skeletal rearrangement. In agreement with this formulation, the compound showed no n.m.r. signal corresponding to aliphatic hydrogen and, unlike X, it was stable at its melting point.

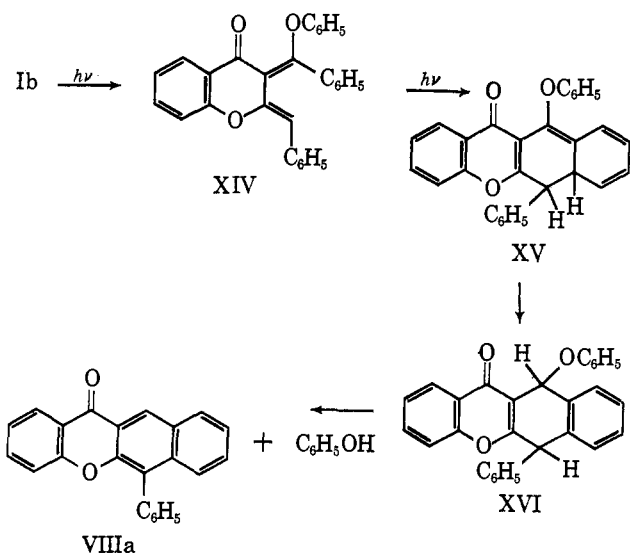


Mechanistic Evidence and Discussion

The above results show that the principal pathway of photodegradation of the chromones I in inert media is through photocyclization of their enols II. Similar reactions such as the conversion of *cis*-stilbene to phenanthrene have been frequently observed.^{3,7} The stilbene reaction has been shown to proceed through a singlet state.^{7d} The principal photocyclization reactions observed in the present study, IIa \rightarrow III and IIb \rightarrow VIIIb, likewise appear to proceed through singlet states since attempts to generate III and VIIIb by benzophenone-sensitized irradiation of the enols II were unsuccessful. It is noteworthy that these two predominant modes of cyclization of the enols are not strictly analogous since it is the hydroxybenzylidene phenyl in IIa that is involved in the cyclization reaction whereas it is the benzhydrylidene phenyl of IIb that undergoes cyclization.

Of particular interest in regard to the cyclization reactions is the formation of the phenylbenzoxanthenone VIIIa, which arises by irradiation of the benzhydrylchromone Ib. While it is difficult to rationalize the formation of this product by initial cyclization of the photoenol IIb, a possible reaction pathway involving phenyl migration to oxygen in the chromone Ib might be envisaged, Ib \rightarrow XIV. Light-induced 1,5-phenyl

(7) (a) H. Stobbe, *Ber.*, **40**, 3372 (1907); (b) F. G. Badder, L. S. El-Assal, and M. Gindy, *J. Chem. Soc.*, 1270 (1948); (c) G. J. Fonken, *Chem. Ind. (London)*, 1327 (1962); (d) F. B. Mallory, C. S. Wood, and J. T. Gordon, *J. Am. Chem. Soc.*, **86**, 3094 (1964), and references cited therein.



migration from a carbonyl carbon to an oxygen of a second carbonyl grouping has previously been observed,⁸ although this would appear to be the first example of such a phenyl migration from a saturated center. If this step is postulated, the subsequent steps XIV \rightarrow XV \rightarrow XVI find close analogy in the above described reaction sequence IIa \rightarrow III \rightarrow IV. The last step, XVI \rightarrow VIIIa, requires the elimination of phenol, which was indeed detected in a separate experiment in a yield comparable to that of VIIIa.

The observation that the benzylchromone Ia underwent ready photoreduction in ethanol or isopropyl alcohol was unexpected. Previous workers have found that *o*-alkylbenzophenones that can undergo photoenolization are exceptionally stable toward irradiation in alcohols.⁹ Since both the photopinacol reduction of benzophenones¹⁰ and the photoenolization of *o*-alkylbenzophenones¹¹ have been shown to proceed by way of triplets, the inhibition of the pinacol reduction by an *o*-alkyl group appears to be due to successful competition of internal over external hydrogen abstraction by the triplet intermediate. In order to determine what factors are responsible for the different behavior of the chromone Ia, the effect of sensitizers and quenchers on the photochemistry of Ia was investigated.

Surprisingly, photolysis of a benzene solution $5.3 \times 10^{-3} M$ in Ia which contained sufficient benzophenone to absorb 99% of the light led to a greatly reduced apparent rate of enol IIa formation over that observed in the unsensitized reaction. This was found to be due to incursion of a previously unobserved back reaction (*vide infra*) which led to a photostationary state that was very poor in enol (enol absorptivity at $460 m\mu = 0.10$). The same photostationary concentration of the enol was also reached upon irradiation of a similar solution in which an initially high concentration of the enol had been generated photochemically

(8) (a) G. W. Griffin and E. J. O'Connell, *J. Am. Chem. Soc.*, **84**, 4148 (1962); (b) H. E. Zimmerman, H. G. C. Durr, R. G. Lewis, and S. Braun, *ibid.*, **84**, 4149 (1962).

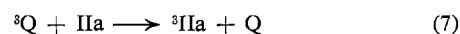
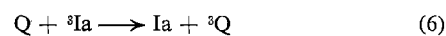
(9) (a) N. C. Yang and C. Rivas, *ibid.*, **83**, 2213 (1961); (b) A. Becket and G. Porter, *Trans. Faraday Soc.*, **59**, 2051 (1963).

(10) (a) H. L. J. Bäckström and K. Sandros, *Acta Chem. Scand.*, **14**, 48 (1960); (b) G. S. Hammond and W. M. Moore, *J. Am. Chem. Soc.*, **81**, 6334 (1959); (c) G. Porter and F. Wilkinson, *Trans. Faraday Soc.*, **57**, 1686 (1961).

(11) E. F. Zwicker, L. I. Grossweiner, and N. C. Yang, *J. Am. Chem. Soc.*, **85**, 2671 (1963).

prior to addition of the sensitizer. Therefore, despite this unexpected complication of a back reaction, the photoenolization reaction was thus shown to be capable of proceeding *via* a triplet.¹² However, this observation did not establish that this was necessarily the predominant reaction pathway upon direct absorption of light by the chromone.

When quenching experiments were undertaken using naphthalene ($0.4 M$) in a benzene solution, $4.2 \times 10^{-2} M$ in chromone Ia, the change in absorptivity at $460 m\mu$, due to enol IIa, was very similar to that observed in the sensitization experiments; that is, a photostationary state was again reached which was very low in enol. This result appeared to be due to a combination of two processes, a reduced rate of photoenolization due to partial quenching of triplet Ia (eq. 1-6), and sensitized destruction of the enol IIa (eq. 7-9) by energy transfer from the triplet naphthalene (3Q) formed in the quenching process.¹⁴ The existence



of these two processes was demonstrated by a successful attempt to eliminate one of them. Thus the sensitized back reaction would not be expected to occur if *trans*-stilbene were used as quencher since the triplet of this quencher has a very short effective lifetime ($k_{10} > 1.3 \times 10^7 \text{ sec.}^{-1}$)¹⁵ and should therefore transfer energy only very inefficiently to the enol. As expected, quenching by *trans*-stilbene, unlike naphthalene, led to good linear rates of enol formation which decreased with increasing stilbene concentration and showed no deviations attributable to a back reaction (Figure 3).

(12) Excitation of Ia by benzophenone triplet is implicated in this process since the energy of the lowest singlet of benzophenone lies below that of Ia and thus precludes singlet energy transfer. Singlet excitation of the enol IIa can be ruled out on kinetic grounds. The observed rate of disappearance of IIa was $5 \times 10^{-4}/\epsilon \text{ mole l.}^{-1} \text{ sec.}^{-1}$ when $[\text{IIa}] = 0.3/\epsilon \text{ mole l.}^{-1}$ (where ϵ is the unknown extinction coefficient of the enol at $460 m\mu$). The rate of light absorption (I) by the solution was about $10^{-6} \text{ einstein l.}^{-1} \text{ sec.}^{-1}$. Assuming the rate of singlet energy transfer from benzophenone to IIa is diffusion controlled,¹³ *i.e.*, $k_s \approx 2 \times 10^9 \text{ l. mole}^{-1} \text{ sec.}^{-1}$, and the benzophenone singlet lifetime is $1/k_d \leq 2 \times 10^{-10} \text{ sec.}$,^{10b} then the maximum possible rate of excitation of IIa to its singlet is $I k_s [\text{IIa}] / (k_s [\text{IIa}] + k_d) = 10^{-6} / (1 + 8.3\epsilon) \approx 1.2 \times 10^{-7} / \epsilon \text{ mole l.}^{-1} \text{ sec.}^{-1}$. By contrast the observed rate of disappearance of IIa ($5 \times 10^{-4} / \epsilon \text{ mole l.}^{-1} \text{ sec.}^{-1}$) was 4000 times higher and thus the reaction of IIa must be sensitized by triplet excitation.

(13) W. M. Moore, G. S. Hammond, and R. P. Foss, *J. Am. Chem. Soc.*, **83**, 2789 (1961).

(14) (a) Singlet energy transfer can again be excluded because population of naphthalene singlet is not possible due to the prohibitively high singlet energy of naphthalene relative to that of the chromone Ia and to the lack of absorption of the $3650\text{-}\text{\AA}$. light by naphthalene; (b) since only about 2.5% of the light was absorbed by the enol IIa at the photostationary concentration in this experiment, involvement of IIa in unsensitized reactions was largely avoided.

(15) (a) G. S. Hammond, J. Saltiel, A. A. Lamola, N. J. Turro, J. S. Bradshaw, D. O. Cowan, R. C. Counsell, V. Vogt, and C. Dalton, *J. Am. Chem. Soc.*, **86**, 3197 (1964); (b) E. F. Ullman, *ibid.*, **86**, 5357 (1964).

Moreover, when both *trans*-stilbene (0.4 M) and naphthalene (0.4 M) were used together as quenchers, a good linear rate was also observed (Figure 3) since inhibition of naphthalene sensitization of IIa (eq. 7) was effected by quenching of naphthalene triplets by stilbene (Figure 3).

It can be shown that these quenching data are only consistent with a mechanism for photoenolization that proceeds exclusively via a triplet intermediate with no kinetically important competition from direct enolization of a singlet species. Thus, if in fact photoenolization can only occur if triplet Ia has been populated, the quantum yield Φ_q is defined by eq. 11. If, then, Φ is the quantum yield in the absence of quencher (Q), eq. 12

$$\Phi_q = k_3 k_4 / (k_2 + k_3) (k_4 + k_5 + k_6 [Q]) \quad (11)$$

$$\Phi / \Phi_q = 1 + k_6 [Q] / (k_4 + k_5) \quad (12)$$

predicts a linear relationship between Φ / Φ_q and [Q]. Since this is indeed found to be the case (Figure 4), the assumption of the exclusive operation of a triplet enolization mechanism is confirmed.

Returning now to a consideration of the reason for the unexpected photoreduction reaction, the above sensitization and quenching experiments show that the enolization process must proceed exclusively by way of triplet states. Moreover, since strong quenching of the photoreduction reaction by 0.3 M naphthalene could be observed, this reaction must also proceed at least predominantly by way of a triplet.¹⁶ Excitation of the chromone Ia must therefore lead to a triplet which, unlike the *o*-alkylbenzophenone triplets, cannot abstract hydrogen internally much more rapidly than it can abstract hydrogen from alcohol; or alternatively, excitation of Ia might lead to two chemically distinct triplets only one of which could undergo the enolization reaction.¹⁷

The rate data provide no support for two reactive triplets. Assuming diffusionally controlled quenching of triplet Ia with $k_6 = 2 \times 10^9 \text{ sec.}^{-1}$,¹⁸ the slope of the curve in Figure 4 ($k_6 / (k_4 + k_5)$) gives the rate of disappearance of triplet Ia in benzene as $k_4 + k_5 = 1.7 \times 10^8 \text{ sec.}^{-1}$, and the rate of enolization of the triplet is therefore $k_4 \leq 1.7 \times 10^8 \text{ sec.}^{-1}$. For comparison, triplet benzophenone in isopropyl alcohol is destroyed entirely by hydrogen abstraction from solvent at a rate of about $0.22 \times 10^8 \text{ sec.}^{-1}$.^{10a} Thus, if triplet Ia abstracts hydrogen from solvent at a rate similar to that of benzophenone triplet, the photoreduction could occur with a quantum yield of at least 13%, which is sufficient to account for our observations without the more complicated assumption of two reactive triplet states.

The reason for the relatively less efficient photoenolization by the triplet chromone than the triplet *o*-alkylbenzophenones is not clear. Possibly steric interactions between the benzoyl phenyl and the chromone ring carbonyl oxygen may account for a reduced population

(16) Cf. ref. 10.

(17) Two stereoisomeric triplets having different chemical properties might be formed provided that the chromone to carbonyl bond order is sufficiently increased in the excited state to prevent rapid rotation of the benzoyl grouping. Compare the isomeric triplet states of benzil: W. G. Herkstroeter, J. Saltiel, and G. S. Hammond, *J. Am. Chem. Soc.*, **85**, 482 (1963). Alternatively two nearly isoenergetic triplets might arise by promotion of the nonbonding electron pairs on either of the carbonyl groups.

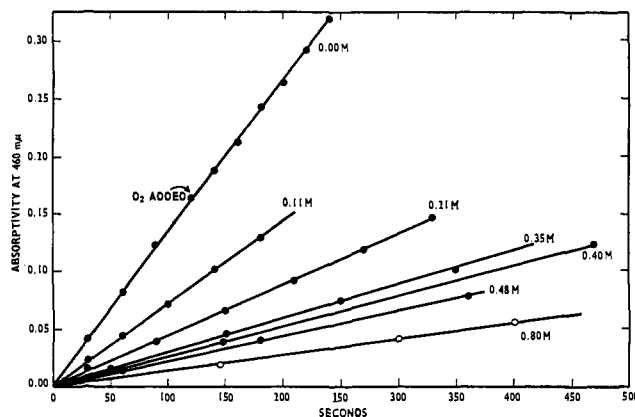


Figure 3. Effect of quencher concentration on the absorptivity at 460 m μ of enol IIa formed by 365-m μ irradiation of a 0.042 M benzene solution of 2-benzyl-3-benzoylchromone (Ia): ●, *trans*-stilbene used as quencher; ○, 0.4 M *trans*-stilbene plus 0.4 M naphthalene used as quencher.

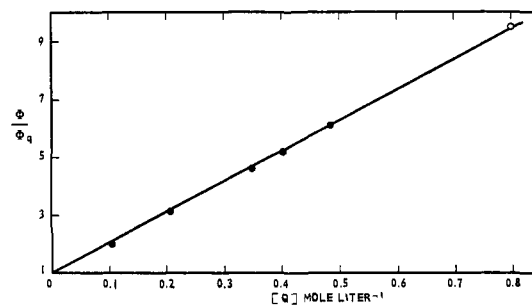


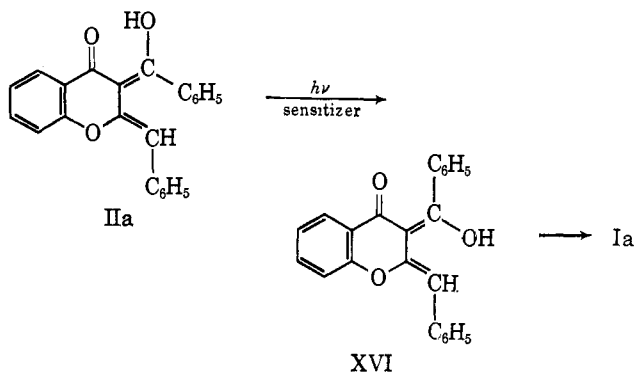
Figure 4. Variation of quantum yield with quencher concentration for photoenolization of a 0.042 M benzene solution of 2-benzyl-3-benzoylchromone (Ia): ●, *trans*-stilbene used as quencher, ○, 0.4 M *trans*-stilbene plus 0.4 M naphthalene used as quencher.

of the configuration of the benzoyl group in ³Ia necessary for internal hydrogen abstraction.

The above observation that the enol IIa is destroyed by a photosensitized process requires additional comment. The product of this reaction was readily shown to be the starting chromone Ia. On irradiation of a chromone solution containing benzophenone for periods sufficient to convert all the chromone to enol, there was no significant change in the photostationary concentration of the enol. The original concentration of chromone could therefore not have changed appreciably, and thus the enol IIa must have given back the chromone in the sensitized reaction. By contrast, direct absorption of light by the enol IIa (population of singlet IIa) gave this reaction inefficiently or not at all. Thus, irradiation of the enol with a visible light source of much greater intensity than the monochromatic source used in the sensitized reaction led to much slower disappearance of the enol than in the sensitized process, and the dihydrobenzoxanthene III was formed. Apparently therefore, *intersystem crossing of singlet IIa must be an exceptionally inefficient process*. It is noteworthy in this regard that it has been suggested that very inefficient intersystem crossing may account for the high photostability of *o*-hydroxybenzophenones, although direct evidence on this point is lacking.^{9b} The present evidence for inefficient crossing in another

hydrogen-bonded ketone lends strong support for this interpretation.¹⁸

The photosensitized ketonization of the enol IIa is probably not a simple, one-step process. The naphthalene quenching experiment, which led to sensitization of the enol by triplet naphthalene formed in the quenching process, demonstrates that the enol triplet is of lower energy than the chromone triplet. The reaction ${}^3\text{IIa} \rightarrow {}^3\text{Ia}$ is therefore energetically improbable, a conclusion which is also supported by evidence implicating the reverse process ${}^3\text{Ia} \rightarrow {}^3\text{IIa}$ in the photoenolization reaction.¹ On the other hand, a photosensitized *cis-trans* isomerization of the enol is an expected consequence of the previously proposed photoenolization mechanism,¹ and it can account by itself for the ketonization reaction. Thus, photoisomerization of IIa to its unstabilized nonhydrogen-bonded isomer XVI should lead to rapid ketonization by a thermal process.



Experimental Section

Light Sources. Two light sources were used for ultraviolet irradiation. The first, used for all the studies but the sensitization and quenching experiments, was an unfocused G.E. B-H6 high-pressure mercury arc equipped with Corning No. 9863 and No. 7740 (6 mm. thick) filters. Transmission was <1% below 310 and above 410 $m\mu$. The distance between the source and the sample was always at least 8 in.

For the sensitization and quenching studies, a Hanovia 100-w. medium-pressure U-shaped mercury vapor arc was used with Corning No. 5860 and No. 7380 filters, which isolated the 365- $m\mu$ line. The sample was contained in a cell held in a fixed position about 6 in. from the unfocused source.

For visible light, a 500-w. Argus No. 540 slide projector was used in conjunction with a Corning No. 3387 cut-off filter. Transmission was <1% below 431 $m\mu$. Sample distance and focus were adjusted to utilize as much of the full light output as practicable.

Effect of Light on 2-Benzyl-3-benzoylchromone (Ia). Irradiation of an Oxygenated Solution with Visible and Ultraviolet Light. A solution of 500 mg. of 2-benzyl-3-benzoylchromone in 500 ml. of benzene was irradiated with visible and ultraviolet light and simultaneously

(18) An expected consequence of the inefficient intersystem crossing of ${}^1\text{IIa}$ is the observation described above that the photoperoxide XI is formed more efficiently by the effect of ultraviolet than of visible light on the enol IIa. Thus direct absorption of light by IIa cannot lead to photooxidation since light-induced cycloaddition reactions of oxygen require sensitization of oxygen by a triplet species.⁶ On the other hand, absorption of light by Ia, which absorbs only in the ultraviolet, will lead to ${}^3\text{Ia}$ which can act as the requisite sensitizing triplet.

bubbled with dry air for 24 hr. The solvent was evaporated from the resulting solution to give a red-orange residue. This was twice recrystallized from heptane-benzene to give 200 mg. of bright orange crystals of *11-hydroxy-6-phenyl-12H-benzo[b]xanthen-12-one* (Va), m.p. 261–263°. Absorption maxima were observed at 229 $m\mu$ ($\log \epsilon$ 4.40), 274 (4.83), 290 (4.42), 316 (4.07), 326 sh (3.50), and 438 (3.74) in the ultraviolet (cyclohexane) and at 3.70 and 6.15 μ in the infrared (CHCl_3). The n.m.r. spectrum displayed signals at τ -4.26 (OH) and at 2.2–2.8 (13 ArH).

Anal. Calcd. for $\text{C}_{23}\text{H}_{14}\text{O}_3$: C, 81.64; H, 4.17; mol. wt., 338. Found: C, 81.76; H, 4.24; *m/e* (parent), 338.

The compound gave a brown-violet color with ferric chloride in aqueous ethanol but gave no color change due to azo coupling on addition of alkali to an ethanolic solution containing benzenediazonium chloride. It also gave a negative Gibbs test,² which was carried out on a solution of the compound in a 1:1 benzene-ethanol mixture because of solubility problems. For comparison, the unsubstituted hydroxybenzoxanthenone Vb was also found to give a positive ferric chloride test, but in addition it produced a dark orange color in the azo coupling reaction and gave a greenish blue color with the Gibbs reagent. Addition of sodium hydroxide to an ethanolic solution of Va caused a shift in the visible absorption maximum from 434 to 470 $m\mu$, which was reversed on addition of acetic acid.

The mother liquors from the recrystallization of Va were evaporated and the residue was chromatographed on neutral alumina. Elution with benzene yielded two components. Recrystallization of the first fraction from acetone gave 17 mg. of *11-phenyl-12H-benzo[b]xanthen-12-one* (VIIa) as greenish yellow needles, m.p. 247–248°. The compound displayed ultraviolet absorption maxima (ethanol) at 238 $m\mu$ ($\log \epsilon$ 4.39), 262 (4.83), 311 (3.81), 323 (3.86), and 390 (3.63), and distinctive infrared maxima (CHCl_3) at 6.04 and 11.94 μ .

Anal. Calcd. for $\text{C}_{23}\text{H}_{14}\text{O}_2$: C, 85.70; H, 4.38; mol. wt., 322. Found: C, 85.79; H, 4.45; *m/e* (parent) 322.

The second component was bright yellow with a brilliant green fluorescence. Recrystallization from ethanol-benzene gave 4.3 mg. of the furan IX, m.p. 211–214°, undepressed on admixture with material prepared by selenium dioxide oxidation of Ia. The ultraviolet and infrared spectra of the compound were identical with those of the synthetic product. By elution of the chromatogram with chloroform, 220 mg. of chromone Ia was recovered.

Simultaneous Irradiation of a Deoxygenated Benzene Solution with Visible and Ultraviolet Light. A solution of 0.500 g. of 2-benzyl-3-benzoylchromone Ia in 50 ml. of benzene was deoxygenated by bubbling with nitrogen. The solution was irradiated for 48 hr. with ultraviolet and visible light to give a deep orange solution containing III. This solution displayed an absorption maximum at 400 $m\mu$. A similarly treated solution in cyclohexane displayed maxima at 249 $m\mu$ ($\log \epsilon$ 3.97), 255 (3.97), 262 (3.95), 274 (3.97), 288 sh (3.85), and 400 (3.52), where the extinction coefficients are based on an assumed 100% conversion of the chromone to III. Upon addition of air to an aliquot of either of these solutions the spectra changed within a

few minutes to that of nearly pure Va (98%, based on starting chromone).

Evaporation of the solvent *in vacuo* from the benzene solution of III gave a material with different spectral properties from those of III, and with a lessened susceptibility toward air oxidation after redissolution in benzene. Since it gave nonintegral n.m.r. signals this material appeared to be a mixture, and further identification was not attempted.

Another benzene solution of III prepared as above was refluxed for 24 hr. under nitrogen. Removal of the solvent *in vacuo* and recrystallization of the residue twice from ethanol gave 0.162 g. of *5a,6-dihydro-11-hydroxy-6-phenyl-12H-benzo[b]xanthen-12-one* (IV) as orange needles, m.p. 204–206°.

Anal. Calcd. for $C_{23}H_{16}O_3$: C, 81.16; H, 4.74. Found: C, 81.39; H, 4.88.

The compound was stable in air as the crystalline solid and in solution in deoxygenated solvents. However, in the presence of air, it oxidized smoothly in solution to give Va in quantitative yield. It displayed absorption maxima at 244 m μ (log ϵ 4.16), 272 (4.30), 294 (4.00), 306 (4.04), 318 (4.08), 330 sh (3.95), and 394 (4.16) in the ultraviolet (cyclohexane), and at 3.33 (OH) and 6.18 (C=O) μ in the infrared (mineral oil). The n.m.r. spectrum ($CDCl_3$) displayed a nonequivalence quartet ($J = 12.0$ c.p.s.) arising from proton resonances at τ 4.53 and 5.54, together with a large aromatic proton signal due in part to partial oxidation during the measurement. The compound gave a brown-violet color with ferric chloride in aqueous ethanol. Addition of sodium hydroxide to an ethanolic solution of IV produced a shift in its visible absorption maximum from 390 to 410 m μ , which was reversed on addition of acetic acid.

Irradiation of an Oxygenated Benzene Solution with Ultraviolet Light. A solution of 1.00 g. of 2-benzyl-3-benzoylchromone (Ia) in 150 ml. of benzene was simultaneously bubbled with dry, benzene-saturated air and irradiated with ultraviolet light for 24 hr. The red solution was then concentrated to a volume of 20 ml. *in vacuo* and 49 mg. of *11-hydroxy-6-phenyl-12H-benzo[b]xanthen-12-one* (Va) was collected by filtration.

Further concentration of the solution to about 13 ml. and addition of hexane gave a precipitate of pale orange crystals. These were recrystallized from benzene-heptane to give 119 mg. of the colorless peroxide X_1 , m.p. 178–180°.

Anal. Calcd. for $C_{23}H_{16}O_5$: C, 74.18; H, 4.33. Found: C, 73.98; H, 4.38.

The peroxide displayed absorption maxima at 263 (sh) m μ (log ϵ 3.75), 296 (3.66), and 303 (3.66) in the ultraviolet (methanol), and at 2.94, 6.10, 6.38, 7.20, and 10.88 μ in the infrared ($CHCl_3$). Singlets were observed in the n.m.r. spectrum ($DMSO-d_6$) at τ 1.82 (OH) and 3.47 (1-H) and an aromatic multiplet was observed at 1.93 to 2.71 (14 H). Addition of deuterium oxide to the n.m.r. sample caused the τ 1.82 peak to disappear.

The compound was not acidic and gave a negative test with ethanolic ferric chloride. It liberated iodine when refluxed with potassium iodide in acetic acid, and gave a deep purple color in an acidified methanolic solution of ferrous ammonium sulfate and ammonium thiocyanate. A peroxide moiety was therefore present.

However, when X_1 was refluxed with potassium iodide and acetic acid in isopropyl alcohol for 2 min., under conditions which are known to reduce hydroperoxides,⁵ no color was observed. Under identical conditions, *t*-butyl hydroperoxide gave a yellow-brown color, while di-*t*-butyl peroxide did not.

On heating the peroxide X_1 above its melting point or on dissolving it in methanol, it rapidly lost water and gave in quantitative yield 2,3-dibenzoylchromone XI, 148–150°, which was shown to be identical with a synthetic sample by mixture melting point and spectral comparison.

The mother liquors remaining after separation of the peroxide X_1 from the photochemical reaction mixture were combined and chromatographed on neutral alumina. The eluate fractions yielded 300 mg. of the chromone Ia and 430 mg. of 2,3-dibenzoylchromone XI, m.p. 148–150°, purified by recrystallization from benzene-heptane.

Anal. Calcd. for $C_{23}H_{14}O_4$: C, 77.96; H, 3.98. Found: C, 78.06; H, 4.36.

The compound displayed absorption maxima at 250 m μ (log ϵ 4.38) and 300 m μ (sh) (log ϵ 3.97) in the ultraviolet (methanol), and at 6.14, 6.34, 7.25, and 10.40 μ in the infrared (chloroform). Only aromatic hydrogen signals were observed in the n.m.r. spectrum. The compound was not acidic and gave a negative ferric chloride test.

Irradiation of a Deoxygenated Ethanol Solution with Ultraviolet Light. A solution of 0.500 g. of 2-benzyl-3-benzoylchromone Ia in 80 ml. of ethanol was deoxygenated by bubbling with nitrogen. After irradiation with ultraviolet light for 30 min., the solution had turned yellow and a white, crystalline precipitate had formed. After 20 hr., the then pale pink precipitate was filtered off (105 mg.). Concentration of the ethanol solution afforded 310 mg. of starting material which was slightly contaminated by the benzoxanthenone Va. The yield of Va, determined spectroscopically, was 3 mg.

The pale pink precipitate was recrystallized from benzene-heptane to give 97 mg. of the colorless reduction product XII, m.p. 190–191°.

Anal. Calcd. for $C_{46}H_{34}O_8$: C, 80.92; H, 5.02; mol. wt., 684. Found: C, 80.64; H, 5.36; mol. wt., 730 (isopiestic method with benzene as solvent).

The infrared spectrum (mineral oil) of this product showed hydrogen-bonded aromatic ketone absorption at 6.18 μ , but lacked the strong maxima typical of the chromone nucleus at 6.10, 7.15, and 10.8 μ .^{4b} In a halocarbon mull, hydrogen-bonded OH absorption was observed at 3.42 μ . The ultraviolet spectrum (cyclohexane) showed peaks at 2.34 m μ (log ϵ 4.72), 264 sh (4.23), 271 (4.23), 280 (4.25), and 306 (4.32). The n.m.r. spectrum (C_6D_6) displayed in addition to aromatic signals a signal at τ 0.38 (OH) and a nonequivalent quartet, double the area of the OH signal, which was calculated to arise from proton resonances at 5.49 and 5.89 ($J = 16.0$ c.p.s.).

The compound gave a negative ferric chloride test and was stable at its melting point under nitrogen. On melting in air, the compound was converted to the chromone Ia, and the air over the melt was reduced in oxygen and increased in water content as shown by mass spectrometry.

11-Hydroxy-12H-benzo[b]xanthen-12-one (Vb). In a test tube were placed 6 g. of naphthalene-1,3-diol, 6 g. of salicylic acid, and 30 g. of ground, freshly fused zinc chloride. The thoroughly mixed materials were heated in a metal bath at 200° for 2 hr. The resultant brown cake was ground in a mortar and extracted successively with water, dilute sodium bicarbonate, and again water. The dried residue was taken up in chloroform and passed through a silica chromatographic column. The yellow fractions so obtained were evaporated and the residue sublimed at 120° (0.2 mm.). The sublimate was recrystallized from ethanol-benzene and then cyclohexane to give 197 mg. of Vb as orange needles, m.p. 198–203°.

Anal. Calcd. for $C_{17}H_{10}O_3$: C, 77.85; H, 3.84; mol. wt., 262. Found: C, 77.97; H, 4.23; *m/e* (parent), 262.

The compound displayed absorption maxima at 226 $m\mu$ (log ϵ 4.44), 269 (4.85), 284 sh (4.42), 309 (4.08), 323 (3.72), and 424 (3.78) in the ultraviolet (cyclohexane) and at 3.70 (OH), 6.12 (C=O), and 12.0 μ in the infrared (chloroform). The n.m.r. spectrum ($CDCl_3$) displayed signals at τ -4.05 (singlet, OH) and 1.70 to 2.97 (aromatic multiplet).

1,3-Diphenyl-9H-furo[3,4-b][1]benzopyran-9-one (IX). A mixture of 0.500 g. of 2-benzyl-3-benzoylchromone (Ia), 0.163 g. of selenium dioxide, and 30 ml. of dry dioxane was heated at reflux for 8 hr. The solution was filtered and the solvent was removed *in vacuo*. A chloroform solution of the residue was extracted three times with aqueous sodium bicarbonate, dried over magnesium sulfate, and evaporated to dryness. Recrystallization of the residue from benzene-ethanol gave 70 mg. (14%) of IX as yellow-green crystals, m.p. 213–214°, strongly fluorescent blue in solution.

Anal. Calcd. for $C_{23}H_{14}O_3$: C, 81.64; H, 4.17. Found: C, 81.81; H, 4.42.

The compound displayed absorption maxima at 264 $m\mu$ (log ϵ 4.38), 294 (4.18), 320 sh (3.99), and 422 (3.81) in the ultraviolet (methanol), and at 5.98 (C=O) and 11.05 μ (very strong) in the infrared (chloroform). Only aromatic hydrogen signals were seen in the n.m.r. spectrum.

2,3-Dibenzoylchromone (XI). A mixture of 0.51 g. of 2-benzyl-3-benzoylchromone Ia, 0.40 g. of chromic anhydride, 0.2 ml. of sulfuric acid, and 25 ml. of glacial acetic acid was refluxed for 16 hr. Filtration gave a green-blue solution, from which the solvent was removed under reduced pressure. A solution of the residue in 30 ml. of chloroform was extracted three times with 10-ml. portions of saturated aqueous sodium bicarbonate and dried. Evaporation of the solvent and recrystallization of the residue from benzene-heptane gave 53 mg. (10%) of XI, m.p. 150–151°.

Effect of Light on 2-Benzhydryl-3-benzoylchromone (Ib). Irradiation of a Deoxygenated Solution with Ultraviolet Light. A deoxygenated solution of 250 mg. of 2-benzhydryl-3-benzoylchromone (Ib) in 25 ml. of benzene was irradiated with ultraviolet light. The solution initially turned deep red, and after 18 hr. it had become a deep yellow. The solvent was evaporated and the residue was chromatographed on neutral alumina. A large yellow fraction was eluted with benzene. The solvent was evaporated and the residue was recrystallized twice from benzene-ethanol to give

181 mg. (76%) of 6,11-diphenyl-12H-benzo[b]xanthen-12-one (VIIb) as lemon yellow needles, melting point and mixture melting point with an independently synthesized sample 232–234°.

Anal. Calcd. for $C_{29}H_{18}O_2$: C, 87.41; H, 4.55; mol. wt., 398. Found: C, 87.54; H, 4.80; *m/e* (parent), 398.

The compound showed absorption at 240 $m\mu$ (log ϵ 4.49), 264 (4.86), 313 (3.82), 326 (3.83), and 403 (3.84) in the ultraviolet (ethanol), and at 6.02 μ (C=O) in the infrared (mineral oil).

Continued elution of the chromatographic column with chloroform gave a second yellow fraction. Evaporation of the solvent and recrystallization from benzene-heptane gave 3.1 mg. (1.6%) of 6-phenyl-12H-benzo[b]xanthen-12-one (VIIIa) as yellow needles, melting point and mixture melting point with an independently synthesized sample 250–255°.

Anal. Calcd. for $C_{23}H_{14}O_2$: C, 85.70; H, 4.38; mol. wt., 322. Found: C, 85.49; H, 4.77; *m/e* (parent), 322.

The compound showed absorption maxima at 240 $m\mu$ (log ϵ 4.46), 263 (4.79), 313 (3.80), 324 (3.84), and 400 (3.66) in the ultraviolet (ethanol), and at 6.04 in the infrared (mineral oil).

Repetition of the above experiment gave, on vapor phase chromatography of a small portion of the original reaction mixture, an amount of phenol corresponding to an estimated 1.1% over-all yield. Similarly, extraction of the bulk of the reaction mixture with aqueous base, acidification of the aqueous extract, and extraction with ether gave about 0.8% of phenol based on mass spectrographic analysis of the ether solution.

Irradiation of an Oxygenated Benzene Solution with Ultraviolet Light. A solution of 127 mg. of 2-benzhydryl-3-benzoylchromone (Ib) in 25 ml. of benzene was bubbled with dry air for 24 hr. during irradiation with ultraviolet light. The solvent was evaporated from the resultant deep orange solution and the residue recrystallized from benzene-ethanol to give 50 mg. (40%) of VIIb. The mother liquor was evaporated and the residue was recrystallized from benzene-heptane to give 30 mg. (21%) of the peroxide XIII as off-white crystals, m.p. 213–215°.

Anal. Calcd. for $C_{29}H_{20}O_5$: C, 77.67; H, 4.50. Found: C, 77.62; H, 4.67.

The compound displayed absorption maxima at 261 (sh) $m\mu$ (log ϵ 3.96), 293 (3.83), and 299 (sh) (3.82) in the ultraviolet (methanol), and at 3.02, 6.13, 6.33, 7.24, and 10.76 μ in the infrared (chloroform), and it displayed only aromatic proton signals in the n.m.r. spectrum. It was not acidic and gave a negative ferric chloride test, and it gave the same positive tests with potassium iodide and with ferrous thiocyanate as did the peroxide X_1 .

6,11-Diphenyl-12H-benzo[b]xanthen-12-one. The synthesis of this compound was modeled after the synthesis of xanthenones by Kamel and Schoeb.¹⁹ To a boiling mixture of 2.76 g. of salicylic acid, 5.33 g. of 1,4-diphenyl-2-naphthol,²⁰ and 50 ml. of toluene was

(19) M. Kamel and H. Schoeb, *Tetrahedron*, 20, 491 (1964).

(20) L. I. Smith and H. H. Hoehn, *J. Am. Chem. Soc.*, 63, 1178 (1941).

added over the course of 10 min. 3.8 ml. of phosphorus oxychloride. After 4 hr. of heating, the mixture was cooled and poured into ice water. The toluene layer was separated, washed with aqueous sodium bicarbonate, dried, and evaporated. The residual light tan gum was dissolved in hot ethanol, and was reprecipitated on cooling as an oil, which subsequently partially solidified. This material weighed 3.65 g. and had an infrared spectrum consistent with that expected for *1,4-diphenyl-2-naphthyl salicylate* with peaks at 3.03 (OH) and 5.91 μ (C=O).

This material (1.90 g.) was heated without further purification in an open test tube at 330–340° for 2 hr. Chromatography of the resultant material with benzene on alumina gave a yellow fraction. Evaporation of this fraction and sublimation of the residue at 170° (0.1 mm.) gave 52 mg. of crystals, m.p. 228–230°. Recrystallization of the product from ethanol gave 23 mg. of VIIb, m.p. 232–234°.

6-Phenyl-12H-benzo[b]xanthen-12-one (VIIIa). To a solution of 16.0 g. of 1-phenyl-2-tetralone²¹ in 100 ml. of cymene was added 2.1 g. of 10% palladium on charcoal. The resulting suspension was refluxed for 10 hr., during which time the formation of water was observed in the condenser. The palladium was filtered off and the solvent was removed *in vacuo*. The residual oil was extracted three times with 30-ml. portions of 6% aqueous sodium hydroxide. Acidification of the aqueous solution gave 9.05 g. (58%) of *1-phenyl-2-naphthol* as a light brown oil, which soon crystallized,

(21) H. E. Zaugg, M. Freifelder, and B. W. Horrom, *J. Org. Chem.*, **15**, 1197 (1950).

m.p. 63–67°. Recrystallization from water gave white needles, m.p. 65–67°.

Anal. Calcd. for C₁₆H₁₂O: C, 87.24; H, 5.49. Found: C, 87.04; H, 5.30.

To a boiling solution of 2.26 g. of salicylic acid and 4.0 g. of 1-phenyl-2-naphthol in 60 ml. of toluene was added slowly 3.1 ml. of phosphorus oxychloride. After heating for 4 hr., the mixture was cooled and poured into ice water. The toluene layer was washed successively with sodium bicarbonate solution and water and then dried. Evaporation of the solvent left a residue which was recrystallized from ethanol to give *1-phenyl-2-naphthyl salicylate*, 3.70 g. (66%), as white crystals, m.p. 129–131°. Two additional recrystallizations gave white needles, m.p. 131–132°.

Anal. Calcd. for C₂₃H₁₆O₃: C, 81.16; H, 4.74. Found: C, 81.10; H, 4.85.

In an open test tube, 2.00 g. of the ester was heated at 340–350° for 5 hr. The resulting gum was twice chromatographed by elution with chloroform on alumina. The bright yellow fraction was evaporated to dryness and the residue was sublimed. Recrystallization of the sublimate from acetone–water gave 110 mg. of *6-phenyl-12H-benzo[b]xanthen-12-one (VIIIa)* as yellow-green needles, m.p. 249–254°.

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The Rates of Some Degenerate Rearrangements as Determined by Nuclear Magnetic Resonance Spectroscopy¹

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The rates and the activation parameters have been determined for the degenerate isomerizations of three different symmetrically disubstituted benzofurazan oxides in order to provide evidence for the mechanism of this type of interconversion. The rates of these very rapid processes were deduced from the line shapes of the n.m.r. spectra of the three compounds at various temperatures in the range from –40 to +50°. The positive entropies of activation (ranging from +4 to +6 e.u.), the relatively small energies of activation (ranging from 15.0 to 16.5

kcal./mole), and the correlation of the relative rates with the size of the substituents at the 4- and 7-positions flanking the N₂O₂ grouping are all considered to support an interconversion mechanism that involves ring opening of the furazan oxide to the corresponding o-dinitrosobenzene as the rate-determining step, followed by very rapid recyclization of this symmetrical intermediate to the heterocyclic N-oxide.

Introduction

Evidence that benzofurazan oxides undergo rapid equilibration of the Ia \rightleftharpoons Ib type in solution has been presented recently.⁵ It is generally considered^{5,6} that

(1) Furazan Oxides. V. For part IV see F. B. Mallory, C. S. Wood, and B. M. Hurwitz, *J. Org. Chem.*, **29**, 2605 (1964).

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(5) (a) G. Englert, *Z. Elektrochem.*, **65**, 854 (1961); (b) P. Diehl, H. A. Christ, and F. B. Mallory, *Helv. Chim. Acta*, **45**, 504 (1962); (c) F. B. Mallory and C. S. Wood, *J. Org. Chem.*, **27**, 4109 (1962);