Photoisomerization of 3-Aroyl-2-(2-furyl)chromones. An Example of Quenching of a Photochemical Reaction by a Product

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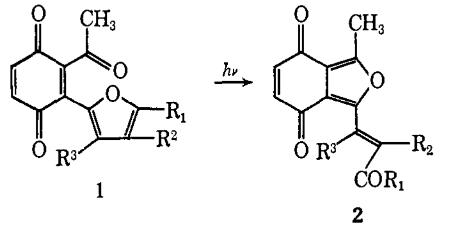
Abstract: Several 3-aroyl-2-(2-furyl)chromones (**6**) were synthesized and subjected to ultraviolet irradiation. At spectroscopic concentrations (10^{-5}–10^{-4} *M*) these compounds undergo photoisomerization to give the 1-arylfuro[3,4-*b*]chromone-3-acrolein system (**7**) in good conversion, but at higher concentrations the conversion is poor. Measurements of the rate of formation of the *p*-anisyl compound (**7b**) from **6b** with respect to the concentration of **7b** indicate that the photoreaction is quenched by the product. The effect of known triplet sensitizers and quenchers indicates that the reaction proceeds predominantly *via* triplet **6b**, and the efficient quenching of this triplet by the product causes the observed concentration dependence.

The efficient photochemical rearrangement of 2-acetyl-3-(2-furyl)benzoquinones (**1**) to the furoquinones (**2**), reported by Weisgerber and Eugster,[1] suggested to us the possible use of a related reaction for the photochemical generation of substituted furo[3,4-*b*]chromones. Apparently, the only previous known example of this latter ring system is the 1,3-diphenyl compound **9**.[2] We report here an investigation of the photolysis of 3-aroyl-2-(2-furyl)chromones (**6**) to the isomeric furo[3,4-*b*]chromones **7**, in which a seldom observed quenching effect was encountered.



1

2

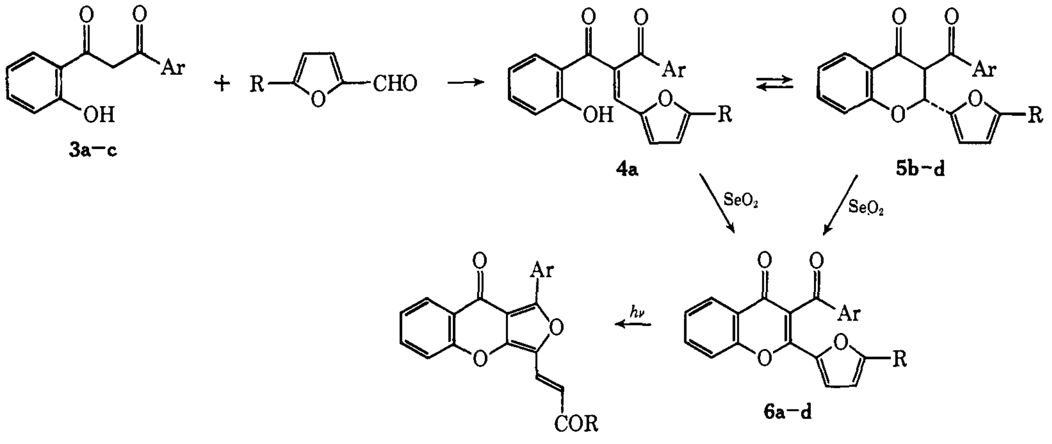
R = H or CH$_3$

Results

The preparation of compounds **6a–d** (Chart I) was carried out according to a known synthesis of 3-aroylflavones,[3] using 2-furanaldehydes in place of the benzaldehyde derivatives employed previously. The structure of the condensation product **4a** was confirmed by infrared and nmr spectra. Oxidation of **4a** with selenium dioxide gave **6a** in excellent yield.

The same sequence of reactions was used to prepare the analogs **6b, c, d**. Here, however, the infrared spectra of the intermediates (two carbonyl bands between 5.85 and 6.05 μ) did not agree with structure **4**, but instead suggested the cyclic structure **5**. This was confirmed by the nmr spectra, which showed, in the case of **5b**, for example, the two ring protons as an AB pattern centered at τ 3.94 and 4.72 (J = 10.5 Hz). On the basis of published nmr data of flavanone compounds,[4] the high coupling constant reflects the expected *trans* orientation of the 2 and 3 substituents in **5b**. The earlier investigators[3] apparently did not examine the possibility

Chart I



3a–c

4a

5b–d

6a–d

7a–d

a, Ar = Ph; R = H

b, Ar = *p*-MeO—Ph; R = H

c, Ar = 3,4,5-tri-MeO—Ph; R = H

d, Ar = *p*-MeO—Ph; R = CH$_3$

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(1) G. Weisgerber and C. H. Eugster, *Helv. Chim. Acta*, **49**, 1806 (1966).

(2) W. A. Henderson, Jr., and E. F. Ullman, *J. Amer. Chem. Soc.*, **87**, 5424 (1965).

(3) W. Baker and F. Glockling, *J. Chem. Soc.*, 2759 (1950).

(4) J. Massicot and J-P. Marthe, *Bull. Soc. Chim. France*, 1962 (1962).

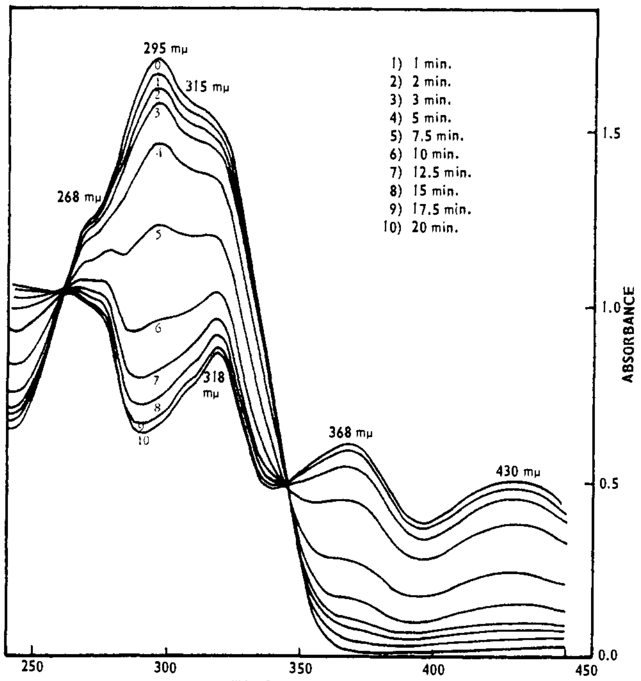
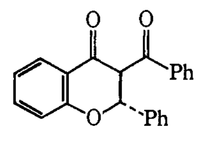


Figure 1. Photolysis of 6.1 × 10^{-5} *M* **6b** in methylene chloride with 240–400-mμ light.

that their condensation products might have the cyclic 3-aroylflavanone structures instead of the assigned open structures analogous to **4a**.[5] Repetition of the reaction between **3a** and benzaldehyde showed by ir and nmr spectroscopy (Experimental Section), however, that this product possessed the cyclic structure **8**. Many of the analogous products that have been reported[3] may also be of a cyclic nature. It is likely, however, that these oxidations, regardless of the structure of the isolated species, proceed by attack of selenium dioxide on the 3-acylchromanone tautomer.



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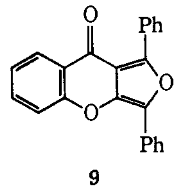

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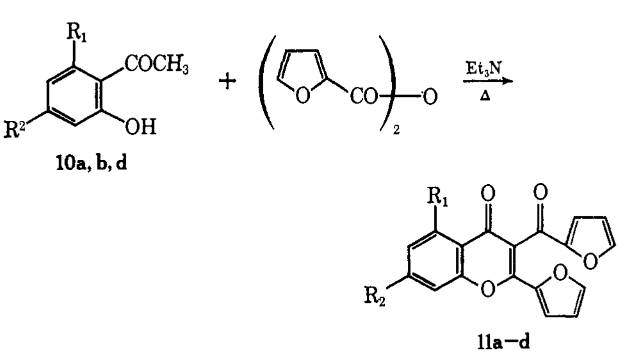
A second synthetic route to 3-aroyl-2-(2-furyl)chromones, based on another literature preparation of 3-benzoylflavone,[6] involves a simple one-step condensation of an *o*-hydroxyacetophenone (**10**) with 2-furoic anhydride. This procedure is limited to the preparation of compounds containing identical substituents at the 2 and Ar positions of formula **6**. Compounds **11a** and **11b** were prepared directly by this technique, while the reaction of 2,6-dihydroxyacetophenone (**10d**) with 2-furoic anhydride was accompanied by esterification of the second hydroxyl group to give **11c**. Acid hydrolysis of the latter then afforded the 5-hydroxychromone **11d**. We were unable to repeat a recently reported preparation[7] of **11d** from **10d** and 2-furoyl chloride; however, the fact that the cited melting point of **11d** was some 40° lower than the value obtained in the present work (*cf.* Experimental Section) indicates that the report may be erroneous.



10a, b, d

11a–d

a, $R_1 = R_2 = H$
b, $R_1 = H; R_2 = CH_3O$
c, R_1 = 2-furoyloxy; $R_2 = H$
d, $R_1 = OH; R_2 = H$

Ultraviolet irradiation of dilute solutions of **6a–d** and **11a–c** resulted in slow generation of yellow colors accompanied by intense green fluorescence. The spectral properties of these solutions (Table I) were consistent with those expected for the furochromone derivatives **7**. The data in Table I were obtained in methylene chloride. This solvent afforded somewhat faster and cleaner conversions to products than some of the other solvents that were examined, such as methanol, acetonitrile, or benzene. The solutions of the chromones, approximately 5 × 10^{-5} *M*, were irradiated with 240–400-mμ light from a 1000-W high-pressure mercury arc until very little change occurred upon further exposure. Under these conditions compounds **6b**, **6c**, and **11a** appeared to be smoothly converted to rearranged products as witnessed by the production of nearly clean isosbestic points, as exemplified by Figure 1. On the other hand, compounds **6a**, **6d**, **11b**, and **11c** did not afford isosbestic points and the interference of side reactions in all of the compounds became noticeable when visible light was not filtered out or when methanol was used as solvent.[8] The 5-hydroxy compound, **11d**, did not give colored or fluorescent products upon irradiation. Examination of

Table I. Spectral Data for 3-Aroyl-2-(2-furyl)chromones

Compd	$\lambda_{max}^{CH_2Cl_2}$ (log ε), mμ	$\lambda_{max}^{CH_2Cl_2}$ of product, mμ
6a	253 (4.37), 317 (4.43)	353, 410
6b	268 sh (4.81), 295 (4.45), 315 sh (4.40)	368, 430
6c	267 (4.17), 311 (4.52)	375, 430
6d	270 sh (4.30), 293 (4.38), 335 (4.37)	430
11a	269 sh (4.34), 282 (4.38), 315 (4.42)	370, 425
11b	262 sh (4.45), 281 (4.56), 316 (4.60)	371, 417
11c	265 (4.45), 319 (4.38)	370, 430
11d	283 (4.49), 321 (4.28)	*a*

[a] Product not observed.

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(5) For a discussion of this type of equilibrium in the simpler *o*-hydroxychalcone–flavanone series see F. M. Dean, "Naturally Occurring Oxygen Ring Compounds," Butterworth and Co., Ltd., London, 1963, p 335 ff.

(6) A. T. M. Dunne, *et al.*, *J. Chem. Soc.*, 1252 (1950).

(7) A. V. Subba Rao and N. V. Subba Rao, *Current Sci.*, **35**, 149 (1966).

(8) Reaction of the furoquinones **2** with alcohols, both in the presence and absence of light, was also noted; see ref 1.

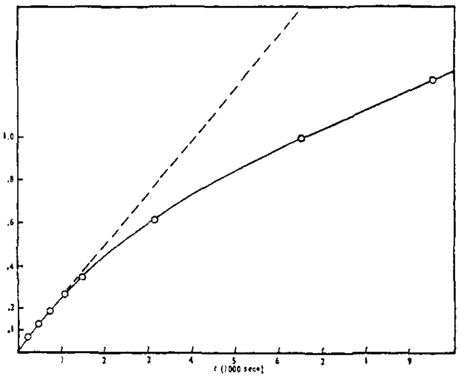

Figure 2. Plot of optical density of **7b** at 430 mμ *vs.* time of irradiation of 1.02 × 10^{-3} *M* **6b** in CH_2Cl_2 with 313-mμ light.

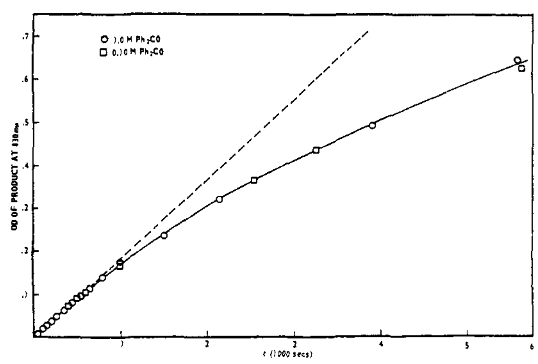

Figure 3. Photolysis of 1.02 × 10^3 *M* **6b** in CH_2Cl_2 sensitized with benzophenone and irradiated with 365-mμ light.

the ultraviolet spectrum showed that little or no reaction had occurred. This lack of photoreactivity, common to a variety of *o*-hydroxy aromatic ketones, probably stems from the rapid deactivation, through internal conversion, of the excited state.[9]

Of the compounds studied, the *p*-methoxybenzoyl derivative **6b** appeared to rearrange most smoothly. For this reason, **6b** was chosen for a more detailed study of the photochemistry of this system, involving product isolation, quantum yield determinations, and sensitization and quenching studies.

From the initial product isolation experiments it was found that the rearrangement of **6b** on a preparative scale proceeded with very low per cent conversion. Irradiation of a 10^{-2} *M* solution of **6b** in benzene with 240–400-mμ light from a 100-W medium-pressure mercury lamp for 24 hr resulted in a 97% recovery of the starting material. A similar experiment run in a Rayonet chamber reactor (peak emission at 300 mμ) afforded an 86% recovery of crystalline **6b**. As these results implied the existence of a severe concentration-dependent quenching effect, the preparative experiments were then repeated at higher dilution (1 × 10^{-4} *M*) approaching the spectroscopic concentrations. Under these conditions the reaction went much further toward completion and a 36% yield of crystalline **7b** was isolated.

The infrared spectrum of this product showed carbonyl bands at 5.97 and 6.17 μ, and the electronic absorption spectrum displayed the long wavelength band at 430 mμ (ε 14,700) in good agreement with the absorption of the model compound **9** at 421 mμ (ε 12,300). The fluorescence emission spectra of **7b** ($\lambda^{\mathrm{Fl}}_{\mathrm{max}}$ 520 mμ) and **9** ($\lambda^{\mathrm{Fl}}_{\mathrm{max}}$ ~525 mμ) in methylene chloride were also very similar. The mass spectrum of **7b** showed the expected parent peak at 346 and the fragmentation pattern was reasonable for the assigned structure. The presence of the acrolein moiety in **7b** was confirmed by the nmr spectrum which also indicated that the orientation around the double bond was *trans*. The three protons in question appeared as an AMX system with a large coupling between the two olefinic protons (J = 15.5 Hz), the same features which appeared in the nmr spectrum of **2** ($R_1 = R_2 = R_3 = H$) to which the *trans* configuration was also assigned.[1] All of the spectral results are thus consistent with the assignment of structure **7b** to the photoisomer of **6b**. Isolation of products from photolysis of the related 3-aroyl-2-(2-furyl)chromones **6a, c, d** and **11a, b, c** was not attempted, but from the spectral data in Table I, it is apparent that similar photoisomerization reactions occur in each case.

Compound **7b** appeared to be stable in methylene chloride or chloroform when stored or heated in the dark. Upon irradiation with intense ultraviolet light, solutions of **7b** were bleached only slowly either in the presence or absence of oxygen. Visible irradiation was more effective in causing photobleaching, especially in the presence of oxygen. Although the nature of the decomposition products is not known, there was no spectral evidence for the formation of **6b**, indicating lack of reversibility for the photoisomerization. In the analogous quinone series Weisgerber and Eugster[1] isolated dimeric by-products containing cyclobutane rings which were formed by light-induced dimerization across the acrolein C–C double bond of **2**. Similar side reactions may occur to some extent in the present case, but photooxidation is probably a more serious problem.

Mechanistic Results and Discussion

Preliminary determinations of the quantum yield of formation of **7b** from **6b** with 3130-Å light were carried out on *nondegassed* solutions at concentrations varying from 10^{-2} to 10^{-4} *M* **6b** in methylene chloride, benzene, or acetonitrile. These ϕ values, which were obtained from the initial slopes of plots of optical density of product at the visible absorption maximum *vs.* time of irradiation, varied from 0.0043 to 0.0071; however, no relationship between the quantum yield and the concentration of **6b** was discernible. The highly inefficient and seemingly concentration-dependent conversion of **6b** to **7b** in the preparative runs appeared at first to be inconsistent with the quantum yields at low conversion. Further investigation under spectroscopic conditions showed a rapid falloff in the rate of product formation, significantly greater than could be accounted for by light absorption by the product, as each photolysis was continued. This was particularly noticeable in the studies at 10^{-2} *M* concentration, where the reaction slowed markedly at conversions of less than 1%, but it was also readily apparent on extended photolysis of even the more dilute solutions.

The initial quantum yield of formation of **7b**, measured on a *degassed* 10^{-3} *M* solution of **6b** in methylene chloride with 3130-Å light, was found to be 0.013, while a value of ϕ = 0.044 was obtained for the benzophenone-sensitized reaction using 3650-Å light under other-

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(9) A. A. Lamola and L. J. Sharp, *J. Phys. Chem.*, **70**, 2634 (1966).

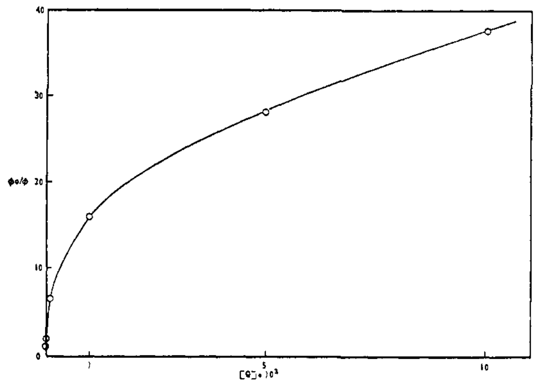

Figure 4. Quenching of formation of **7b** from **6b** by anthracene in CH_2Cl_2.

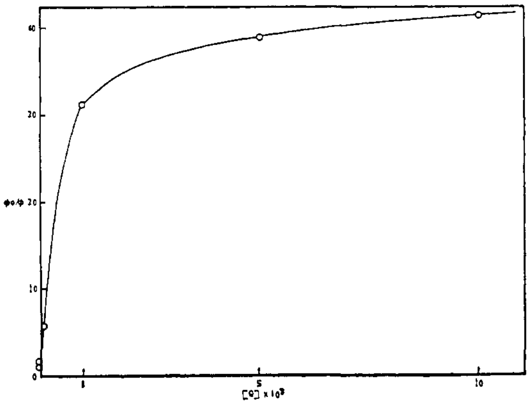

Figure 5. Quenching of formation of **7b** from **6b** by *trans*-1,3,5-hexatriene in CH_2Cl_2.

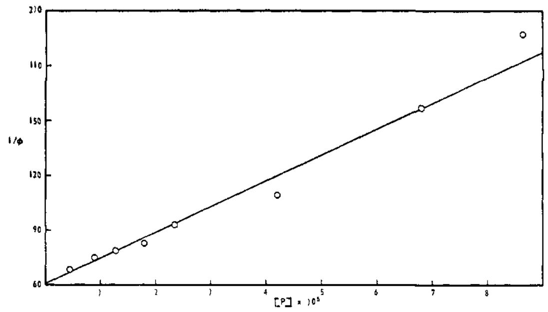

Figure 6. Photolysis of 1.02×10^{-3} *M* **6b** in methylene chloride with 313-mμ light. The final three points are corrected for light absorption by product.

wise similar conditions. In addition to showing the deleterious effect of oxygen, these results show that the reaction can be sensitized with a known triplet sensitizer (E_T = 69 kcal/mole) and the shapes of the curves (Figures 2 and 3) illustrate that a similar rate reduction occurs with time in both the sensitized and unsensitized reactions. Thus, the process responsible for the rate of product formation falling off, as the reaction proceeds, most probably involves triplets.

The effect of known triplet quenchers on the photochemical conversion of **6b** to **7b** was therefore investigated. Although the photoreaction was quenched by 1,3-cyclohexadiene (E_T = 53.5 kcal/mole),[10] rather high concentrations of the diene were required for efficient quenching. Anthracene (E_T = 42 kcal/mole)[11] was much more efficient in this respect; even at concentrations as low as 1×10^{-5} *M* it caused a *ca.* 50% reduction in the initial rate of formation of **7b**. A plot of ϕ_0/ϕ *vs.* anthracene concentration (Stern–Volmer plot, Figure 4) was, however, not linear. Such results usually are interpreted to mean that part of the reaction proceeds *via* an excited state which is not quenched, that is, a state other than the lowest triplet.[12] The results of quenching the photolysis of **6b** with *trans*-1,3,5-hexatriene (E_T = 47 kcal/mole)[10] were very similar to those obtained with anthracene. The Stern–Volmer plot (Figure 5) was of similar shape and each curve indicated that about 2% of the reaction proceeded by a nonquenchable route, most probably through the singlet. The quenched portions of these reactions were estimated from the initial slopes of Figures 4 and 5 to have $k_q\tau_0$ values of roughly 5×10^4 l./mole.

Since both the sensitization and quenching studies indicate that this photochemical transformation proceeds primarily *via* a triplet, or series of triplets, the most reasonable interpretation of the rate data then is that the rate-controlling triplet[13] is efficiently quenched by the product **7b**. As such a process depends directly upon the concentration of product [P], an inverse relationship between the concentration of starting material and the per cent conversion to product would be expected and is indeed observed.

Instances of quenching of a reactant triplet by a photochemical product, while seldom reported, are not unknown; indeed, they may be more common than generally realized. One example of this phenomenon is the photolysis of acetone vapor, studied by Heicklen and Noyes,[14] in which the photoproduct biacetyl quenched both the photodecomposition and the phosphorescence of the acetone. More recently, Frank[15] found that the acetophenone-sensitized photolysis of α-pinene in the absence of solvent, a reaction which proceeds with very high initial quantum yield, ceases at approximately 20% conversion, apparently due to quenching by the products. While other less clearcut examples have also been mentioned, we are unaware of any specific discussion of this phenomenon.

A study was made to see if a more quantitative basis for assignment of triplet energy transfer to product could be made in this system. The product concentration [P] determined spectroscopically at the end of small intervals during a photolysis was used in the Stern–Volmer equation (1) as the concentration of the quencher

$$\phi_0/\phi = 1 + k_q\tau_0[P] \qquad (1)$$

during those intervals. In this equation ϕ_0 is the quantum yield in the absence of quencher, k_q is the rate constant for quenching, and τ_0 is the lifetime of the excited species in the absence of the quencher. While numer-

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(10) D. F. Evans, *J. Chem. Soc.*, 1735 (1960).

(11) S. P. McGlynn, T. Azumi, and M. Kasha, *J. Chem. Phys.*, **40**, 507 (1964).

(12) See, for example, P. J. Wagner and G. S. Hammond, *J. Amer. Chem. Soc.*, **87**, 4009 (1965); **88**, 1245 (1966).

(13) It should be pointed out that the product **7b**, in addition to quenching triplet **6b** or the triplet of the sensitizer, if present, may also quench the triplet of some intermediate. We assume that in the direct photolysis triplet **6b** transfers its energy to **7b**; however, in view of the demonstrated evidence for an intermediate (see below), it is conceivable that it is an intermediate triplet that transfers its energy to **7b**.

(14) J. Heicklen and W. A. Noyes, Jr., *J. Amer. Chem. Soc.*, **81**, 3858 (1959).

(15) G. Frank, *J. Chem. Soc.*, *B*, 130 (1968).

ical values for k_q and τ_0 are often not available, they are assumed to be constants in a given system. Plotting the reciprocal of the quantum yield ϕ for the interval involved *vs.* the product concentration at the end of each interval gave a good linear relationship as shown in Figure 6, demonstrating the efficiency of the product as a quencher. A similar examination of the product concentration and quantum yield reciprocal also revealed a linear relationship in the benzophenone-sensitized reaction (Figure 7) providing conclusive evidence of the triplet quenching nature of the process. This line was independent of the benzophenone concentration as long as the latter absorbed virtually all the light. The ϕ_0 values were calculated from the intercepts to be 0.016 for direct photolysis and 0.049 for the sensitized reaction, in close agreement with the 0.013 and 0.044 values obtained from Figures 2 and 3. The calculated value of $k_q\tau_0$ for quenching by **7b** in the unsensitized reaction is 2.4×10^4 l./mole and thus the rate constant k_q for quenching by product is of the same order as that for quenching by anthracene or *trans*-1,3,5-hexatriene.

The data for the decrease in quantum yield as a function of the increasing concentration of product in both the sensitized and unsensitized reactions also fit well to the expression (2) which relates apparent quantum

$$1/\phi_{\mathrm{app}} = 1/\phi_0 + k_q[\mathrm{P}]/2fk_r \qquad (2)$$

yield at any particular point in the reaction to the product concentration at that point, with the product assumed to behave as a triplet quencher. In this treatment $\phi_{\mathrm{app}} = [\mathrm{P}]/I_0t$, I_0 = light intensity, t = time, f is the intersystem crossing ratio, and k_r and k_q are the rate constants for conversion of triplet to product and quenching by product, respectively. This expression is derived by considering the pertinent processes at photochemical equilibrium to produce the steady-state approximation

$$\frac{\mathrm{d}}{\mathrm{d}t}{}^3R = fI_0 - k_r{}^3R - k_q{}^3RP - k_d{}^3R = 0 \qquad (3)$$

where ${}^3R$ is the steady state concentration of the reactant triplet intermediate. Thus

$$\frac{\mathrm{d}P}{\mathrm{d}t} = k_r{}^3R = \frac{fI_0k_r}{k_r + k_d + k_qP} \qquad (4)$$

Integrating over the range of product concentration and time and defining $\phi_0 = fk_r/(k_r + k_d)$, where $P = 0$, leads directly to eq 2. The relationship of (2) to (1) can readily be shown by substitution for ϕ_0 in (1) and also substituting $(1/k_r + k_d)$ for τ_0 to get (2) without the integration factor.

All of these results are thus consistent with the view that the conversion of **6b** to **7b** proceeds primarily *via* triplet **6b** and that the quenching of this process by the product **7b** causes the apparent concentration dependence.[13] The triplet energy of **6b** was determined to be 57.5 kcal/mole from its phosphorescence spectrum, measured at 77°K in a 2-methyltetrahydrofuran glass. The structured emission spectrum showed a vibrational spacing (~1600 cm^{-1}) consistent with n,π* carbonyl emission with the 0–0 band at 497 mμ. Although the triplet energy of **7b** could not be measured due to its lack of phosphorescence, it is undoubtedly less than 57.5 kcal/mole since its lowest singlet energy is only ~61 kcal/mole, and thus the energetics of the system favor quenching. In the quinone series studied by Eugster[1] the triplet levels may well be reversed, that is, the products may have higher triplet energies than the starting materials, so that quenching does not occur and high conversion is not prevented.

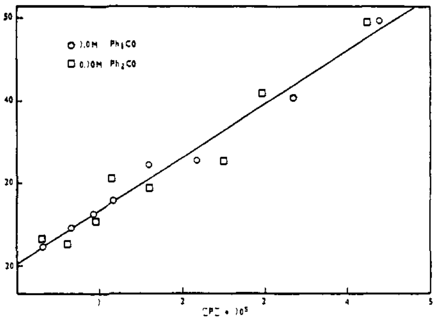

Figure 7. Photolysis of 1.02×10^{-3} *M* **6b** in methylene chloride sensitized with benzophenone at 365 mμ.

While the results obtained thus far do not fully delineate the mechanism of the photoisomerization of the 3-aroyl-2-(2-furyl)chromones, some possible intermediates in this transformation are shown in Chart II. Although discussion of these intermediates is necessarily speculative, some evidence for the existence of a discrete intermediate has been found and precedent for each of these structures does exist. For example, we have previously observed a transient 2H-pyran species similar to i from irradiation of an *o*-alkenylbenzophenone and, in addition, we have observed photochemical transformations of the latter which seem to require an intermediate formally analogous to ii.[16] Srinivasan[17] has reported photochemical reactions of furan and simple alkylfurans in which the first step very probably corresponds to formation of an intermediate cyclopropenecarboxaldehyde as in iii. A 2–5 bridging of a five-membered ring heterocycle, as in iv, has been proposed as the first step in the photoisomerization of certain imidazoles,[18] while the photochemical fragmentation of epoxides to carbenes and carbonyl compounds (iv → v) has been well documented.[19] It should be noted that each of the postulated reaction pathways involves more than one photochemical step in the over-all scheme. This is consistent with our observation that the conversion of **6b** to **7b** is intensity dependent. For example, a 67.5% reduction in the intensity of incident light by means of a neutral density gradient screen caused a decrease in the *quantum yield* of formation of **7b** of approximately 40%. A trivial process such as initial formation of the *cis* isomer of **7b** which would then require a second photon for conversion to the *trans* product may be responsible. On the other hand, the *trans* **7b** could be generated directly *via* excited states and one of the other postulated intermediates may require further photoexcitation. Despite much effort, no intermediate could be detected spectroscopically at room temperature and the visible absorption bands of pure **7b** and the solutions obtained after low

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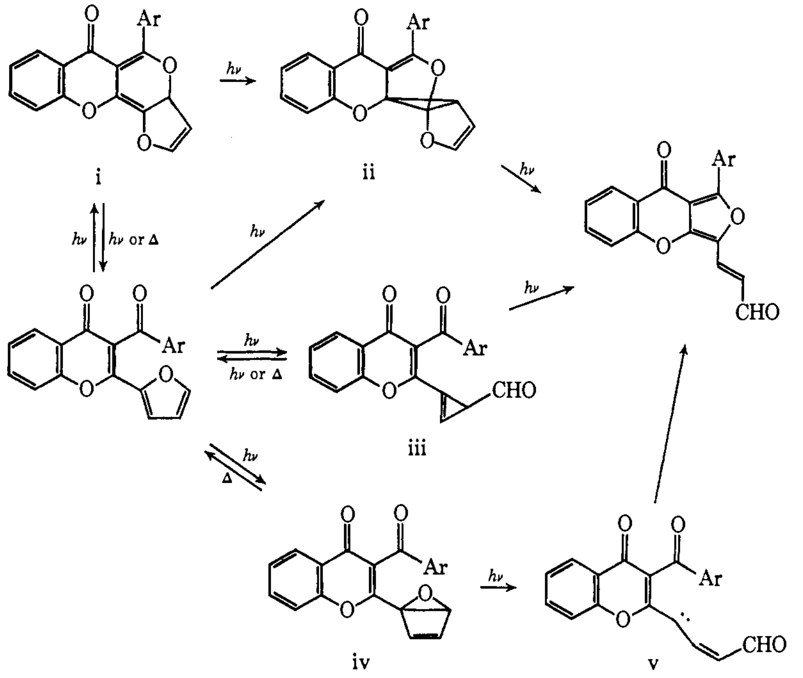
(16) K. R. Huffman and E. F. Ullman, *J. Amer. Chem. Soc.*, **89**, 5629 (1967).

(17) (a) R. Srinivasan, *ibid.*, **89**, 1758 (1967); (b) H. Hiraoka and R. Srinivasan, *ibid.*, **90**, 2720 (1968).

(18) P. Beak, J. L. Miesel, and W. R. Messer, *Tetrahedron Letters*, 5315 (1967).

(19) P. C. Petrellis, H. Dietrich, E. Meyer, and G. W. Griffin, *J. Amer. Chem. Soc.*, **89**, 1967 (1967).

Chart II



conversions of **6b** to product were the same. However, irradiation (240–400 mμ) of a concentrated solution of **6b** in 2-methyltetrahydrofuran at −196° imparted a faint yellow color to the glass which faded upon warming to about 0°. When a similar experiment was performed on a frozen 1×10^{-5} *M* solution of **6b** in 2-methyltetrahydrofuran at −164° it was found that the long-wavelength absorption bands of **6b** gradually decreased in intensity upon irradiation. After warming to −80° for 1 hr and subsequent recooling to −164° these bands increased in intensity, apparently reversing about 40% of the original decrease. Since fluorescence was not observed at any stage of this procedure, the final product **7b** could not be present, indicating the photochemical formation of a labile species which thermally reverts back to **6b**. The nature of this species, or whether it is in fact a true intermediate in the conversion of **6b** to **7b**, remains undetermined. An attempt to observe this transient by the use of infrared spectroscopy was unsuccessful due to the low conversion of starting material.

Experimental Section[20]

The qualitative photochemical studies were performed using a 1000-W General Electric B-H6 high-pressure mercury arc equipped with Corning No. 9863 nickel oxide (transmission 240–400 mμ) or Pyrex glass (transmission >300 mμ) filters or a combination of the two (300–400 mμ). The quantum yield determinations were performed with a 100-W Hanovia mercury lamp which was calibrated according to the method of Hatchard and Parker.[21] The 365-mμ line was isolated by the use of Corning No. 5860 and 7380 filters and the 313-mμ line with potassium chromate and Corning No. 9863 filters. Solutions were degassed by the freeze–pump–thaw technique and the sensitizers and quenchers were purified by recrystallization or distillation before use.

Condensation of Aldehydes with *o*-Hydroxydibenzoylmethanes. General Procedure. Compounds **4a** and **5b,c,d**, were prepared following the method of Baker and Glockling.[3] A solution of 0.010 mole of the *o*-hydroxydibenzoylmethane, 0.011 mole of the aldehyde, and several drops of piperidine in 50 ml of ethanol was refluxed for 30 min to 2 hr. The product which separated upon cooling was recrystallized from ethanol.

2-Furfurylidene-1-(*o*-hydroxyphenyl)-3-phenyl-1,3-propanedione (4a). Reaction of *o*-hydroxydibenzoylmethane[22] with furfural afforded an 80% yield of **4a**, mp 154.5–159°; $\lambda_{\max}^{\text{mull}}$ 6.22 μ.

Anal. Calcd for $C_{20}H_{14}O_4$: C, 75.46; H, 4.43. Found: C, 75.49; H, 4.45.

***trans*-3-(*p*-Anisoyl)-2-(2-furyl)-4-chromanone (5b).** *o*-Hydroxy-*p*′-methoxydibenzoylmethane[3] and furfural gave **5b** in 59% yield, mp 127–130°. Recrystallization from methanol–water afforded tan crystals, mp 136.5–140°; $\lambda_{\max}^{\text{mull}}$ 5.97, 6.03 μ. The nmr spectrum showed the aliphatic ring protons as a pair of doublets centered at τ 3.94 and 4.72 (*J* = 10.5 Hz).

Anal. Calcd for $C_{21}H_{16}O_5$: C, 72.40; H, 4.63. Found: C, 72.39; H, 4.64.

***trans*-3-(3,4,5-Trimethoxybenzoyl)-2-(2-furyl)-4-chromanone (5c).** Compound **5c** was obtained from 2-hydroxy-3′,4′,5′-trimethoxydibenzoylmethane[3] and furfural. The yield was 65%, mp 114–115.5°. Recrystallization from ethanol gave a mixture of crystalline modifications, mp 113–143°. Two further recrystallizations raised the melting point to 129–145°; $\lambda_{\max}^{\text{mull}}$ 5.86, 6.03 μ.

Anal. Calcd for $C_{23}H_{20}O_7$: C, 67.64; H, 4.94. Found: C, 67.91; H, 4.96.

Solution infrared spectra ($CHCl_3$) of the low- and high-melting samples were identical.

***trans*-3-(*p*-Anisoyl)-2-(5-methyl-2-furyl)-4-chromanone (5d).** This compound was obtained from *o*-hydroxy-*p*′-methoxydibenzoylmethane (**3b**) and 5-methylfurfural in 81% yield: mp 134–136.5°; $\lambda_{\max}^{\text{mull}}$ 5.92, 6.04 μ. The analytical sample separated as pale yellow needles, mp 137–140°.

Anal. Calcd for $C_{22}H_{18}O_5$: C, 72.92; H, 5.01. Found: C, 72.98; H, 4.94.

***trans*-3-Benzoylflavanone (8).** The reaction of **3a** with benzaldehyde was carried out according to the literature procedure[3] to give a 76% yield of white solid, mp 154–158°, after one recrystallization. A purified sample, mp 157.6–160° (lit.[3] mp 158–160°), showed $\lambda_{\max}^{\text{mull}}$ 5.90 and 5.98 μ. The nmr spectrum showed an AB pattern centered at τ 3.96 and 4.85 (*J* = 12 Hz). Selenium dioxide oxidation of **8** gave 3-benzoylflavone, mp 131–133° (lit.[3] mp 130–131°).

3-Benzoyl-2-(2-furyl)chromone (6a). A mixture of 320 mg of **4a** and 220 mg of selenium dioxide in 10 ml of dioxane was refluxed for 6 hr, filtered, and evaporated to dryness. The resulting solid recrystallized from ethanol to give 310 mg (97%) of **6a** as tan crystals, mp 214.5–215°.

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[20] All nmr spectra were measured in deuteriochloroform. Infrared spectra were run in mineral oil suspensions, unless otherwise noted. Melting points are corrected.

[21] C. G. Hatchard and C. A. Parker, *Proc. Roy. Soc.* (London), **A235**, 518 (1956).

[22] T. S. Wheeler, *Org. Syn.*, **32**, 72 (1952).

Anal. Calcd for $C_{20}H_{12}O_4$: C, 75.94; H, 3.82. Found: C, 75.52; H, 3.77.

3-(*p*-Anisoyl)-2-(2-furyl)chromone (6b). The above procedure, applied to **5b**, afforded the chromone **6b** in 83% yield, mp 171–173°. Recrystallization from ethanol afforded cream colored crystals with a double mp of 144–146 and 172.5–173.5°.

Anal. Calcd for $C_{21}H_{14}O_5$: C, 72.83; H, 4.07. Found: C, 73.01; H, 4.07.

In a large scale run a different crystalline modification, mp 165–166.5°, was obtained using the identical procedure. Solution spectra of the two forms were indistinguishable.

3-(3,4,5-Trimethoxybenzoyl)-2-(2-furyl)chromone (6c). Oxidation of **5c**, as above, afforded a 94% yield of **6c**, mp 160–161.5°. The analytical sample was obtained as colorless crystals, mp 161–162°, from ethanol.

Anal. Calcd for $C_{23}H_{18}O_7$: C, 67.97; H, 4.46. Found: C, 68.14; H, 4.47.

3-(*p*-Anisoyl)-2-(5-methyl-2-furyl)chromone (6d). A mixture of 1.81 g of **5d** and 0.61 g of selenium dioxide in 40 ml of dioxane was refluxed for 6 hr to give 1.51 g (84%) of **6d**, mp 167–169°.

Anal. Calcd for $C_{22}H_{16}O_5$: C, 73.32; H, 4.48. Found: C, 73.25; H, 4.35.

3-(2-Furoyl)-2-(2-furyl)chromone (11a). A mixture of 0.68 g (0.005 mole) of *o*-hydroxyacetophenone, 4.95 g (0.024 mole) of 2-furoic anhydride,[23] and 1.5 g (0.015 mole) of triethylamine was heated at 175–180° for 5 hr. The cooled black oil was treated with 1:1 methylene chloride–ether and the insoluble product was filtered. The filtrate was washed twice with 5% Na_2CO_3, dried, and evaporated and a second crop was crystallized in the same manner. One recrystallization of the combined crops from ethanol gave 0.83 g (54%) of **11a**, mp 212–213°. A second recrystallization from methanol using charcoal afforded tan crystals, mp 214–215°.

Anal. Calcd for $C_{18}H_{10}O_5$: C, 70.59; H, 3.29. Found: C, 70.73; H, 3.37.

3-(2-Furoyl)-2-(2-furyl)-7-methoxychromone (11b). A mixture of 0.83 g of *o*-hydroxy-*p*-methoxyacetophenone, 4.1 g of 2-furoic anhydride, and 1.5 g of triethylamine was heated at 150° for 6 hr and worked up as in the preceding example. The chromone **11b** was obtained as a tan solid, 0.36 g (21%), mp 234–235°.

Anal. Calcd for $C_{19}H_{12}O_6$: C, 67.85; H, 3.60. Found: C, 67.37; H, 3.67.

3-(2-Furoyl)-5-(2-furoyloxy)-2-(2-furyl)chromone (11c). A mixture of 0.75 g of 2,6-dihydroxyacetophenone, 5.0 g of 2-furoic anhydride, and 1.5 g of triethylamine was heated at 160° for 4 hr. The resulting black solid mass was triturated with 2:1 methylene chloride–ether to give 1.85 g (89%) of **11c** as light brown crystals, mp 252–253°. Trituration with boiling methanol gave tan crystals of the same melting point: $\lambda_{\max}^{\text{mull}}$ 5.75, 5.99, 6.12 μ.

Anal. Calcd for $C_{23}H_{12}O_8$: C, 66.35; H, 2.91. Found: C, 66.70; H, 2.98.

3-(2-Furoyl)-2-(2-furyl)-5-hydroxychromone ((11d). A suspension of 0.42 g of **11c** in 35 ml of acetic acid and 25 ml of concentrated HCl was refluxed for 6 hr. The resulting clear solution was poured into ice water to give 0.31 g (95%) of **11d**, mp 202–212°. Two recrystallizations from water raised the melting point to 211.5–214.5°; $\lambda_{\max}^{\text{mull}}$ 5.98, 6.08 μ.

Anal. Calcd for $C_{18}H_{10}O_6$: C, 67.08; H, 3.13. Found: C, 66.83; H, 3.17.

Photolysis of 3-(*p*-Anisoyl)-2-(2-furyl)chromone. Isolation of 7b. A solution of 24 mg of **6b** in 700 ml of methylene chloride in a quartz vessel was flushed with nitrogen for 30 min, stoppered, and irradiated in a Rayonet chamber reactor equipped with 16 bulbs having peak emission at 300 mμ. After 45-min irradiation the solution was concentrated *in vacuo* and combined with the product solutions of three similar runs. The combined solutions were evaporated to dryness and the resulting orange-brown gum was crystallized by slow evaporation from methylene chloride–petroleum ether to give 35 mg (36%) of crude **7b**, mp 195–210° dec. One recrystallization from the same solvent mixture afforded dark orange crystals: mp 208–213°; $\lambda_{\max}^{\text{mull}}$ 5.97 and 6.17 μ; $\lambda_{\max}^{CH_2Cl_2}$ 264 (18,600), 273 (18,700), 318 (19,750), 368 (15,100), and 430 mμ (14,700).

Anal. Calcd for $C_{21}H_{14}O_5 \cdot 0.5H_2O$: C, 70.98; H, 4.25. Found: C, 70.52; H, 4.15.

1,3-Diphenylfuro[3,4-*b*]chromone (9). A solution of 463 mg of 3-benzoyl-2-(α-bromobenzyl)chromone[24] in 15 ml of acetic acid containing 0.5 ml of 48% hydrobomic acid was refluxed for 1.5 hr. The orange solution was treated with a few drops of water and allowed to cool. The yellow crystalline solid was filtered and washed with water, 261 mg (70%), mp 209–210°. The infrared spectrum was identical with that of a previous sample of **9**.[2]

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[24] K. R. Huffman, M. Loy, W. A. Henderson, Jr., and E. F. Ullman, *J. Org. Chem.*, **33**, 3469 (1968).