Phototransformations of Benzopyranols and Related Systems. Steady-State and Laser Flash Photolysis Studies[1]

D. Ramaiah,[2a] P. M. Scaria,[2a] D. R. Cyr,[2b,c] P. K. Das,*[2b] and M. V. George*[2a,b]

Department of Chemistry, Indian Institute of Technology, Kanpur 208016, India, and Radiation Laboratory and Department of Chemistry, University of Notre Dame, Notre Dame, Indiana 46556

Received August 19, 1987

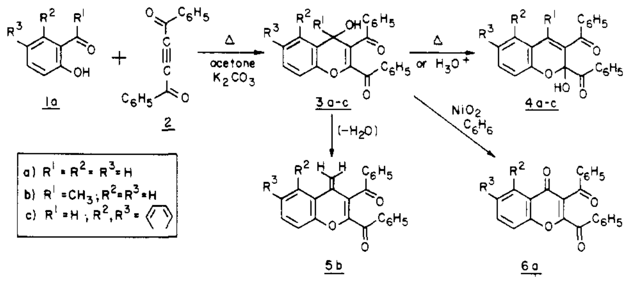
The phototransformations of several 4-benzopyranol systems incorporating the 1,2-dibenzoylalkene moiety have been studied by steady-state photolysis, product analysis, and nanosecond laser flash photolysis. Under direct photolysis, prototropic reactions leading to 2-pyranols and/or their methoxy analogues are shown to dominate, presumably through the intermediacy of carbocations produced as a result of photodehydroxylation. No products, e.g., butenoic acid/ester derivatives, attributable to intramolecular phenyl group migration along the 1,2-dibenzoylalkene moiety, are observed. The laser flash photolysis of 4- and 2-pyranols in benzene or methanol shows the formation of triplets, characterized by unusually short lifetimes (submicrosecond), which testify to the reactive nature of the triplets. In addition, in the case of 2-pyranols, longer-lived transient species characterized by absorptions at long wavelengths (700–800 nm) are observed; these are best assigned as biradicals, produced as a result of ring-opening via triplet-mediated C_2–O bond cleavage.

Introduction

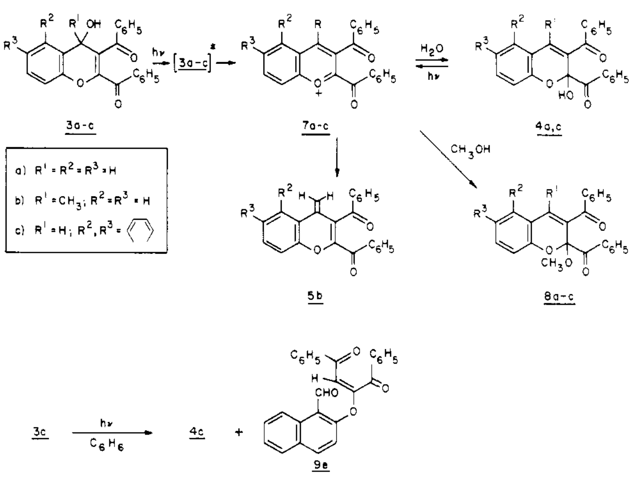
Earlier, we examined the phototransformations of several multichromophoric substrates containing 1,2-dibenzoylalkene moieties such as 1,4- and 1,2-epoxy compounds,[3,4] dibenzobarrelenes,[4-8] 1-pyrazolyl-1,2i-dibenzoylalkenes,[9,10] 1-aziridinyl-1,2-dibenzoylalkenes,[11] 1-imidazolyl-1,2-dibenzoylalkenes,[12] and epoxyindanone adducts.[13] In general, it has been observed that the photorearrangements of substituted 1,2-dibenzoylalkenes depend strongly on the nature of the substituents. For example, dibenzobarrelenes[4-8] containing the 1,2-dibenzoylalkene chromophore undergo the di-π-methane rearrangement (Zimmerman rearrangement),[14] giving rise to dibenzoyl-substituted dibenzosemibullvalenes and not the 1,2-dibenzoylalkene rearrangement.[15,16]

In the present work, we have examined by steady-state and laser flash photolysis phototransformations of some representative 4*H*-1-benzopyran-4-ols and 2*H*-1-benzopyran-2-ols incorporating the 1,2-dibenzoylalkene moiety. The object has been to characterize the photoproducts formed and to elucidate the pathways through which they evolve. Recently reported examples[17] of adiabatic photodehydroxylation reactions of 9-phenylxanthen-9-ol and related substrates prompted us to undertake this photochemical study.

Scheme I



Scheme II



Results and Discussion

1. Preparative Chemistry. The starting substrates, 4*H*-1-benzopyran-4-ols **3a–c**, were prepared in yields ranging between 63% and 86% through the nucleophilic addition of the appropriate *o*-hydroxy carbonyl compounds **1a–c** to dibenzoylacetylene (DBA, **2**) in the presence of

---

[1] Document No. NDRL-3025 from the Notre Dame Radiation Laboratory.

[2] (a) Indian Institute of Technology. (b) University of Notre Dame. (c) Undergraduate research student from the University of Waterloo, Ontario, Canada.

[3] Murty, B. A. R. C.; Kumar, C. V.; Dabral, V.; Das, P. K.; George, M. V. *J. Org. Chem.* **1984**, *49*, 4165–4171.

[4] Murty, B. A. R. C. Ph.D. Thesis, Indian Institute of Technology, Kanpur, 1982.

[5] Kumar, C. V. Ph.D. Thesis, Indian Institute of Technology, Kanpur, 1981.

[6] Kumar, C. V.; Murty, B. A. R. C.; Lahiri, S.; Chackachery, E.; Scaiano, J. C.; George, M. V. *J. Org. Chem.* **1984**, *49*, 4923–2939.

[7] Murty, B. A. R. C.; Pratapan, S.; Kumar, C. V.; Das, P. K.; George, M. V. *J. Org. Chem.* **1985**, *50*, 2533–2535.

[8] Pratapan, S.; Ashok, K.; Cyr, D. R.; Das, P. K.; George, M. V. *J. Org. Chem.* **1987**, *52*, 5512–5517.

[9] Lohray, B. B.; Kumar, C. V.; Das, P. K.; George, M. V. *J. Org. Chem.* **1984**, *49*, 4647–4656.

[10] Lohray, B. B. Ph.D. Thesis, Indian Institute of Technology, Kanpur, 1983.

[11] Barik, R.; Kumar, C. V.; Das, P. K.; George, M. V. *J. Org. Chem.* **1985**, *50*, 4309–4317.

[12] Barik, R.; Bhattacharyya, K.; Das, P. K.; George, M. V. *J. Org. Chem.* **1986**, *51*, 3420–3428.

[13] Ramaiah, D.; Rajadurai, S.; Das, P. K.; George, M. V. *J. Org. Chem.* **1987**, *52*, 1082–1089.

[14] Zimmerman, H. E. In *Rearrangements in Ground and Excited States*; de Mayo, P., Ed.; Academic: New York, 1980; Vol. 3, pp 131–166.

[15] Griffin, G. W.; O'Connel, E. J. *J. Am. Chem. Soc.* **1962**, *84*, 4148–4149.

[16] Zimmerman, H. E.; Dürr, H. G. C.; Lewis, R. G.; Braun, S. *J. Am. Chem. Soc.* **1962**, *84*, 4149–4150.

[17] (a) Wan, P.; Yates, K.; Boyd, M. K. *J. Org. Chem.* **1985**, *50*, 2881–2886. (b) Wan, P.; Yates, K. *Rev. Chem. Intermed.* **1984**, *5*, 157–181.

0022-3263/88/1953-2016$01.50/0

anhydrous potassium carbonate at room temperature in a suitable solvent such as acetone (Scheme I). The 2*H*-1-benzopyran-2-ol (**4a**) was prepared in a 58% yield by the treatment of **1a** with **2** in refluxing acetone containing potassium carbonate. The benzopyranone **6a** was prepared through nickel peroxide oxidation of **3a** (96%) in benzene at room temperature, whereas the 4-methylene-4*H*-1-benzopyran **5b** (60%) was the product of the acid-catalyzed dehydration of **3b**. The structures of **3a–c**, **4a**, **6a**, and **5b** were established on the basis of analytical results, spectral evidence, and chemical transformations, wherever possible.

The UV spectrum of **3a** in methanol showed absorption maxima at 253 nm (ϵ 20000), 279 (9850, sh), and 298 (6400, sh), respectively. The absorption maxima, however, shifted to 272 nm (ϵ 22900) and 391 (20850), when **3a** was dissolved in 10 M H_2SO_4 (aqueous), indicating thereby that the benzopyrylium cation **7a** was formed under these conditions. The UV spectrum of **4a** in methanol showed absorption maxima at 245 nm (ϵ 23600), 300 (14400), and 345 (7400), whereas the spectrum of **4a** in 10 M H_2SO_4 (aqueous) showed absorption maxima at 272 nm (ϵ 23700) and 391 (21300). Note that the UV spectra of **3a** and **4a** in strong sulfuric acid are practically identical. The UV spectrum of **4a** in strongly alkaline medium such as methanolic sodium hydroxide (0.7 N) showed absorption maxima at 238 nm (ϵ 12100), 310 (8300), 332 (12100), and 460 (4100). It is reasonable that in the strongly alkaline medium, **4a** is converted to the phenoxide ion as a result of base-catalyzed ring-opening.[18]

2. Steady-State Photolysis. The irradiation (RPR 3000 Å) of **3a** in benzene and acetone gave **4a** exclusively in 65% and 74% yields, respectively, whereas that of **3a** in methanol gave a mixture of **4a** (52%) and **8a** (10%) (Scheme II). The photolysis of **3b** in benzene, acetone, and methanol gave the anhydro product, namely, 2,3-dibenzoyl-4-methylene-4*H*-1-benzopyran (**5b**), in 63%, 55%, and 62% yield, respectively. The irradiation of **3c** in benzene, on the other hand, gave a mixture of **4c** (44%) and (*E*)-1-(1-formyl-2-naphthoxy)-1,2-dibenzoylethylene (**9c**, 20%); the same compound (**3c**) in acetone gave exclusively **4c** (85%). The photolysis of **3c** in methanol led to a mixture of **4c** (40%) and 2,3-dibenzoyl-3-methoxy-3*H*-naphtho[2,1-*b*]pyran (**8c**). When the 2*H*-1-benzopyran-2-ol **4a** was subjected to photolysis in methanol, the methoxy derivative **8a** was obtained in a 36% yield, along with a 30% recovery of the unchanged starting material (**4a**). The structures of all the photoproducts were established on the basis of analytical data, spectral evidence, and chemical evidence, wherever possible. The stereochemistry of **9c** has been assumed to be of the *E* configuration, on the basis of steric considerations and the literature precedents.[19]

The formation of the various products in the course of steady-state photolysis of the benzopyranols **3a–c** and **4a** can be understood in terms of the pathways shown in Scheme II. Photodehydroxylation from the excited state(s) gives carbocations **7a–c**, which act as intermediaries for subsequent transformations to isolated products. Thus, the reaction of carbocations **7a,c** with water leads to the 2*H*-pyran-2-ols **4a,c**, and the cations **7a–c** may be trapped with methanol leading to the corresponding methoxy derivatives **8a–c**. The formation of the anhydro derivative **5b** from **3b** can also be explained in terms of the carbocation intermediate **7b**, which can undergo ready deprotonation under the reaction conditions. It is pertinent to note that in the course of irradiation of the benzopyranols **3a–c** and **4a**, none of the products resulting from 1,2-dibenzoylalkene rearrangement could be observed.

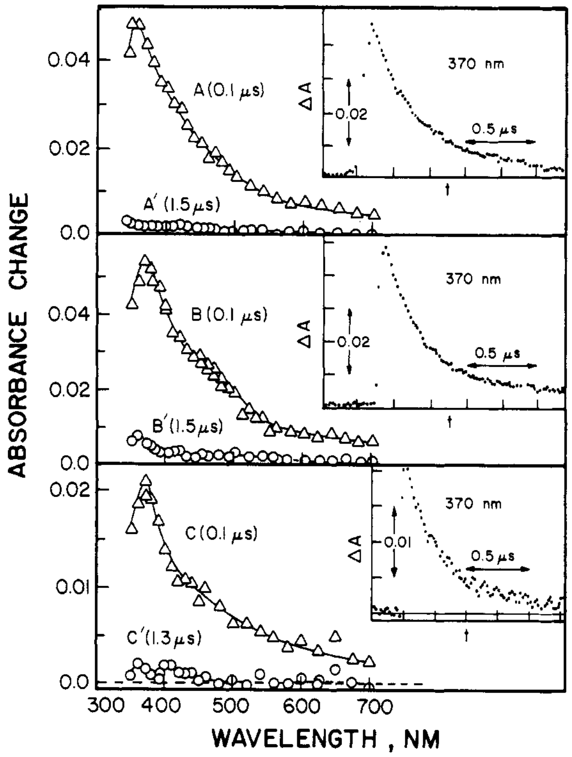


Figure 1. Transient absorption spectra from 337.1-nm laser pulse excitation of (A,A′), **1a**, (B,B′) **1b**, and (C,C′) **1c** in benzene at 295 K. The insets show the kinetic traces at 370 nm in respective cases. The times (after laser flash) at which the spectra were observed are given in the figures.

3. Laser Flash Photolysis Studies. Upon 337.1-nm laser pulse excitation, benzene and methanol solutions of **3a–c** produce short-lived species characterized by submicrosecond lifetimes (τ = 0.2–0.3 μs) and broad absorption spectra (λ_{max} 370–375 nm). The transient absorption spectra and decay traces in benzene are presented in Figure 1. The long-lived residual absorptions at the end of the decay of the fast components (Figure 1) are very weak. On the basis of the following evidence, the short-lived components are assigned to the triplets of the substrates. First, the transients are readily quenched by oxygen, nitroxy radical (4-hydroxy-2,2,6,6-tetramethylpiperidinyl-1-oxy, HTEMPO), and ferrocene, the rate constants for the quenching by ferrocene being in the limit of diffusion control ($k_q = (5.3\text{–}5.9) \times 10^9\ M^{-1}\ s^{-1}$ in benzene). Second, when benzene solutions of **3a–c** containing 0.1–0.5 mM β-carotene are flash-photolyzed at 337.1 nm, growths of transient absorptions at 520–600 nm due to β-carotene triplet are observed, suggesting that triplets acting as excitation donors to the polyene are formed. The kinetics of the formation of β-carotene triplet absorption are faster than, but close to, those of the decay of the 360–370 nm transients from **3a–c**. Note that although in these experiments β-carotene absorbs a substantial fraction of the laser photons (up to 70%), there is practically no triplet formation as a result of the direct excitation of the polyene because of its negligible intersystem crossing efficiency (this is confirmed by blank experiments in which β-carotene solutions were flash-photolyzed in the absence of the substrates). Third, the laser pulse excitation (337.1 nm) of benzophenone (BP) in benzene in the presence of 0.4–2.0 mM **3a–c** shows the enhancement of the decay of BP triplet (monitored at 532 nm); the bimolecular rate con-

---

[18] Gupta, R. K.; George, M. V. *Tetrahedron*, **1975**, *31*, 1263–1275.

[19] Venkataraman, P. S.; Saxena, N. K.; Tripathi, V. K.; Mehta, G. *Indian J. Chem.* **1975**, *13*, 852–854.

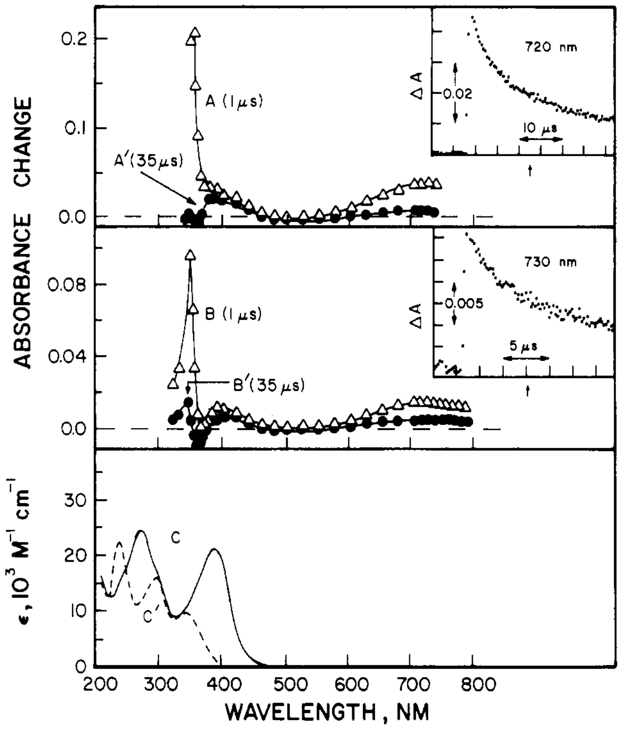


Figure 2. Transient absorption spectra from 337.1-nm laser pulse excitation of **4a** in (A,A′) benzene and (B,B′) methanol at 295 K. The curves C and C′ represent the absorption spectrum of carbocation from **4a** in 10 M H_2SO_4 (see text) and that of **4a** in methanol, respectively. Insets: typical kinetic traces at long wavelengths in benzene (upper) and methanol (lower).

stants for BP triplet quenching by **3a–c** are estimated in the range (3–4) × 10^9 M^{-1} s^{-1}. At relatively high concentrations (1.5–2.0 mM) of **3a,c**, the delayed formation of their short-lived triplets is clearly indicated at 360–450 nm as a result of energy transfer from BP triplet. In these experiments, the ground-state absorbance due to BP at the laser excitation wavelength is relatively high (2.0–3.0 in 2-mm cells at 337.1 nm) so that only ≤20% of the laser photons are absorbed by the substrates (acceptors). Attempts to generate the triplets by energy transfer from camphorquinone (E_T = 52 kcal mol^{-1})[20] proved unsuccessful.

Upon 337.1-nm laser pulse excitation, benzene and methanol solutions of **4a** produce a long-lived transient species characterized by a broad absorption band system at long wavelengths, i.e., 600–800 nm (in addition to sharper and stronger absorptions at 340–370 nm) (see Figure 2). As shown in the insets of Figure 2, the transient decays over microseconds with complex kinetics. In the presence of oxygen, the decay kinetics in methanol become predominantly first order, the observed lifetime being 0.55 μs in air-saturated methanol. On the basis of this lifetime, the rate constant for oxygen quenching is estimated to be 9 × 10^8 M^{-1} s^{-1} in this solvent. In air-saturated benzene also, the decay of the 750-nm species becomes considerably enhanced, although this cannot be fitted well into single-exponential first-order kinetics. Another interesting property of the 750-nm species is that it is quenched by the nitroxy radical, HTEMPO, the rate constant for the quenching being 1.5 × 10^7 M^{-1} s^{-1} (in benzene). On the other hand, the decay behavior of the 750-nm species (in benzene) remains practically unchanged upon addition of ferrocene (up to 6.1 mM), suggesting that it cannot possibly be a triplet with E_T > 40 kcal mol^{-1}.

In order to know if the oxygen quenching of the 750-nm species leads to the formation of singlet oxygen ($^1O_2$*, $^1\Delta_g$), experiments were done in which air-saturated solutions of **4a** in benzene and methanol, and those of BP in benzene, optically matched at 337.1 nm (absorbance = 2.0 in 2-mm cells), were flash-photolyzed at this wavelength in the presence of 0.05 mM diphenylisobenzofuran (DPBF). The bleaching of DPBF as a result of its reaction with $^1O_2$* (endoperoxide formation) was monitored at 420 nm (over ~100 μs). Interestingly, the relative amounts of photogenerated $^1O_2$*, measured in terms of negative absorbance change due to DPBF depletion, was about twice as much in the case of **4a** as in the case of BP. Since the triplet of **4a** is too short-lived to be significantly quenched by oxygen in air-saturated solutions (see later), the oxygen quenching of the 750-nm species appears to be the most reasonable source of $^1O_2$* in the case of **4a**. It should be noted that the bleaching of DPBF in the case of **4a** is not observed in deoxygenated solutions.

The transient behavior of the 750-nm species in mildly acidic and basic conditions was studied using solutions of **4a** in 1:1 H_2O/methanol (v/v). Addition of H_2SO_4 up to 2.0 mM does not affect the decay kinetics of the observed transient species. However, upon gradual addition of NaOH (up to 1.2 mM), the transient absorption at 340–350 nm is seen to undergo progressively enhanced decay. Concomitant to this decay, there is growth of transient absorption at 360–380 nm. From the linear dependence of the pseudo-first-order rate constant for transient absorption decay at 340 nm on [NaOH], the rate constant for the reaction of the 340-nm transient with the base is measured to be 3.0 × 10^8 M^{-1} s^{-1} (in 1:1 H_2O/MeOH, v/v). It should be noted that the ground-state spectrum of **4a** in aqueous methanol does not change in the presence of the low concentration of H_2SO_4 employed, indicating the lack of formation of the carbocation **7a** under this condition. The carbocation **7a** is apparently formed (as shown by the development of a green coloration) when the substrate **4a** is added, as a small quantity of solid or of acetonitrile solution, to strong sulfuric acid (10 M). The resultant absorption spectrum is shown in Figure 2C; the extinction coefficient in this figure is calculated on the basis of the assumptions that the amount of **4a** added to the acid is completely dehydroxylated to the carbocation and that there is no loss of **4a** via side or subsequent reactions. In the weakly alkaline media, i.e., in the presence of NaOH (1.2 mM) in aqueous methanol, **4a** develops a long tail (370–550 nm) beyond its lowest energy absorption band system (λ_{max} 345 nm); the intensity of this tail absorption slowly increases with time (over hours) as the basic solution is allowed to stand in the dark, suggesting that it is due to the product of a thermal reaction of **4a** with the base (most probably, base-catalyzed ring-opening to give the corresponding phenoxide derivative). The laser flash photolysis experiments in the basic media (described above) were carried out within minutes after the addition of NaOH, to ensure that the light absorption at the excitation wavelength (337.1 nm) was still dominated by the unchanged substrate (**4a**).

The monitoring of transient absorption on a short time domain (50–100 ns) following the laser pulse excitation of **4a** in benzene or methanol shows an extremely short-lived species that absorbs at 400–500 nm (λ_{max} ~440 nm). In

---

[20] Evans, T. R.; Leermakers, P. A. *J. Am. Chem. Soc.* **1967**, *89*, 4380–4382.

[21] (a) Gijzeman, O. L. J.; Kaufman, F.; Porter, G. *J. Chem. Soc., Faraday Trans. 2* **1973**, *69*, 727–737. (b) Kuzmin, V. A.; Tatikolov, A. S.; Borisevich, Yu. E. *Chem. Phys. Lett.* **1978**, *53*, 52–55. (c) Kuzimin, V. A.; Tatikolov, A. S. *Chem. Phys. Lett.* **1978**, *53*, 606–610. (d) Watkins, A. R. *Chem. Phys. Lett.* **1980**, *70*, 262–265.

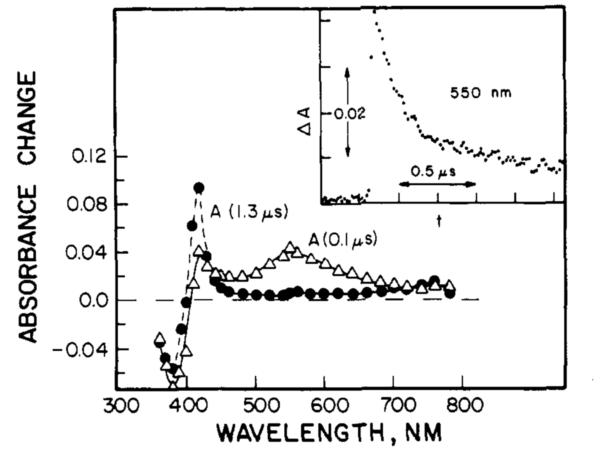


Figure 3. Transient absorption spectra observed at (A) 0.1 and (B) 1.3 µs, following 337.1-nm laser flash excitation of **4c** in benzene at 295 K. Inset: kinetic trace for transient absorption decay at 550 nm.

benzene the decay ($\tau \leq 10$ ns) of this species nearly follows the laser pulse; the decay lifetime is shown to be longer (~20 ns) in methanol. Because of the short lifetime, no quenching studies could be convincingly done to establish the identity of the transient. However, based on the observation of an analogous but longer lived phototransient that is characterized as the triplet of the methoxy derivative **8a** (see later), it seems extremely likely that the 10–20-ns transient observed in the case of **4a** constitutes the triplet of **4a**.

The transient phenomena observed upon 337.1-nm laser flash photolysis of **4c** in benzene and methanol are dominated by a fast-decaying species ($\tau \sim 0.4$ µs) having an absorption maximum at 540 nm; this is followed by a longer lived component ($\tau \sim 85$ µs in benzene), the absorption of which extends to long wavelengths (λ_{max}'s 415–420 and ~750 nm) (Figure 3). Detailed quenching studies on the short-lived component (λ_{max} 540 nm) using oxygen, HTEMPO, and ferrocene establish this to be due to the triplet of **4c**; these kinetic studies also show that the longer lived component is a product of the decay of this triplet (that is, the magnitude of the residual absorption decreases proportionately as the triplet is progressively quenched by ferrocene or HTEMPO). The longer lived component, monitored at 415–420 nm, is also quenched by oxygen and HTEMPO with rate constants of 1.2×10^8 and 1.7×10^7 M^{-1} s^{-1}, respectively (in benzene). This behavior is reminiscent of that observed for the 750-nm species in the case of **4a** (vide supra).

Experiments on the methoxy derivatives **8a,c** similar to those described above for **4a,c**, led to the characterization of their triplets (λ^T_{max} 460 nm for **8a** and 550 nm for **8c**). The triplets of are significantly longer lived than their hydroxy analogues (**4a,c**). Triplet-mediated, longer lived residual absorptions, spectrally similar to those observed in the case of **4a,c** but considerably weaker in intensity, are also observed in the case of **8a,c**. The spectral and kinetic data for the triplets of the various substrates are summarized in Table I.

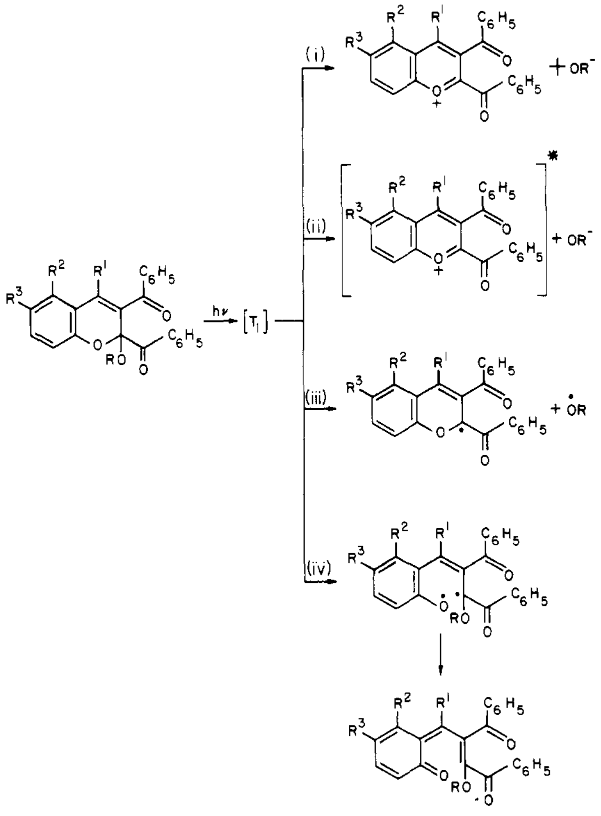
The short lifetimes (submicrosecond) of the benzopyranol triplets reflect their reactive nature. Although each of these molecules has a double bond as a part of the chromophore, twisting about this bond in the triplet state should not be facile because of the constraint imposed by the ring. Also, such a relaxation in the triplet state (if extensive) would manifest itself in the rate constants for quenching by oxygen and ferrocene (that is, k_q^T by O_2 would be relatively high, while k_q^T by ferrocene would be relatively small). In view of the photochemistry observed under steady-state irradiation (described earlier), dehydroxylation to the carbocations appears to be a major photochemical pathway for the decay of the triplets of **3a–c** and **4a,c**.

Table I. Absorption Spectral and Kinetic Properties of Triplets in Benzene at 295 K

substrte	λ_{max}^T, nm[a]	τ^T, µs[b]	$10^9k_q^T$, M^{-1} s^{-1} [c] O_2	HTEMPO	ferrocene
3a	365	0.33 (0.17)	1.2	1.1	5.9
3b	370	0.27 (0.24)	1.1	0.74	5.3
3c	370	0.28 (0.30)	0.97	0.95	5.3
4a	~440	≤0.01 (~0.02)			
4c	460	0.12 (0.15)	1.3	0.54	6.2
8a	540	0.35 (0.43)	1.6	0.69	6.8
8c	550	0.75 (0.98)	1.3	0.08	4.4

[a] ±5 nm. [b] ±15%; the data in parentheses are in methanol. [c] ±15%; the oxygen-quenching rate constants were measured from triplet decay rates in air-saturated benzene (vs those in degassed solutions).

As shown below, one can think of several possible assignments for the long-lived species (600–800 nm) observed in the case of **4a,c** and **8a,c**. Among these, the carbocation assignment (pathway i) seems very likely because of the prototropic photochemistry observed in the course of steady-state photolysis. Note that one would expect the photogenerated carbocations to decay by mixed or second-order kinetics (i.e., by back-reaction with OR^- and/or reaction with hydroxylic solvent molecules). However, a close examination of the results reveals several facts that do not support the carbocation assignment. First, the observed difference spectrum due to the transient species in question in the region of ground-state absorption of **4a** does not agree with that expected on the basis of the difference spectra of **4a** and the carbocation. Specifically at 250–450 nm, the extinction coefficients of the carbocation are much higher than those of **4a** (see Figure 2C,C′), and thus one would expect only positive absorbance change



in this spectral region as a result of the carbocation formation from **4a** (in disagreement with the bleaching observed at ~360 nm in methanol, Figure 2B,B′). Second, the extinction coefficient of the carbocation, as generated from **3a** and **4a** in strong sulfuric acid, is not high enough at 600–800 nm to account for the laser flash photolytic absorbance changes in this region. A comparison of the end-of-pulse absorbance change at 720 nm for **4a** in methanol with that due to benzophenone triplet at 520 nm in acetonitrile produced in optically matched solutions shows that the product of the extinction coefficient and the photochemical yield of the carbocation would have to be $\geq$1200 M^{-1} cm^{-1} in order to be singly responsible for the absorbance changes at the long wavelengths. Since the photochemical yield is $\leq$1.0, this means that the carbocation would have a band system at 600–800 nm with extinction coefficients $\geq$1200 M^{-1} cm^{-1}. There is no way such a strong band system would remain undetected when **3a** or **4a** is dissolved in strong sulfuric acid (5 M). Third, the sensitivity of the decay of observed transients toward oxygen and HTEMPO is unusual for a carbocationic species in the ground state.

As assignment in terms of carbocation triplets (pathway ii) would be interesting because there are precedents of photoadiabatic dehydroxylation in singlet excited state manifolds (e.g., 9-phenylxanthen-9-ol). Note that the triplet formation in triplet manifolds also would be spin allowed. From the onset of absorption of the carbocation from **4a** (at ~460 nm), the singlet energy (most possibly S_1) is estimated at 62 kcal mol^{-1}. It is possible that the triplet energy (T_1) of the carbocation would be higher than the excitation energy of singlet oxygen ($^1O_2^*$, $^1\Delta_g$), and hence the quenching of carbocation triplets by $^3O_2$ may occur by an energy-transfer mechanism. Thus, the formation of singlet oxygen as a result of the oxygen quenching of the 750 nm transient in the case of **4a** becomes explainable. The quenching by HTEMPO can also be explained by the spin-exchange mechanism.[2] However, on the following grounds, we are reluctant to accept the carbocation triplet assignment. First, since the carbocation triplets from **4a** and **8a** would be identical, their interaction with the base (OH^-) should occur in a similar manner. In practice, experiments with **8a** in the presence of 0.4–0.8 mM NaOH in aqueous methanol do not show the decay/formation phenomena at 340–370 nm, as observed in the case of **4a**. Second, an experiment was performed in which an attempt was made to sensitize the formation of the carbocation triplet. A methanolic solution of a mixture of **4a** and erythrosin B (absorbances = 2.1 at 308 nm and 0.20 at 532 nm) was flash-photolyzed sequentially by two laser pulses at the two wavelengths, the second pulse (532 nm) being delayed by 14 μs relative to the first one (308 nm). At 308 nm, >95% of the laser photons was absorbed by **4a**, giving rise to the 750-nm species, which decayed to the extent of ~80% during the period (14 μs) before the arrival of the 532-nm laser pulse. The 532-nm laser pulse predominantly photolyzed the dye producing its triplet (E_T = 44 kcal mol^{-1}),[22] which was monitored at 600 nm. Although the decay of the dye triplet was found to be enhanced when the first laser pulse (308 nm) was used to photolyze **4a** (relative to the case in which **4a** was not photolyzed), there was no indication for delayed formation of the 750-nm species as a result of possible energy transfer from the dye triplet to the carbocation.

For two reasons, we rule out the interpretation in terms of radicals derived from $^{\bullet}$OR cleavage (pathway iii). First, one would not expect such radicals in the ground state to generate $^1O_2^*$ as a result of interaction with $^3O_2$. Second, for **4a** in methanol, the $^{\bullet}$OH radical should react with the solvent, producing the reducing radical, $^{\bullet}CH_2OH$; the formation of the latter should be detectable by its reaction with paraquat, PQ^{2+} (methyl viologen).[23] In laser flash experiments with **4a** in the presence of 0.2–1 mM PQ^{2+} in methanol (λ_{exc} 337.1 nm), no growths of transient absorption due to the semireduced radical, $PQ^{\bullet+}$ (λ_{max} 395 and 615 nm) were observed at either absorption maximum.

Finally, we are left with the assignment in terms of biradicals produced from C_2–O bond cleavage (pathway iv). Such biradicals would represent the lowest triplet excited states of the corresponding photoenols (or enol ethers) and may potentially interact with $^3O_2^*$ (by an energy-transfer mechanism) and a nitroxy radical (by a spin-exchange mechanism). Also, the differences in the acid–base behaviors of the transients from **4a** and **8a** become readily explainable in terms of the ketyl center at C_2 in the phototransient from **4a**. The fact that we do not observe electron transfer from this transient (i.e., from the ketyl radical site) to PQ^{2+} is not disturbing, because the ketyl radicals from aromatic α-diketones (e.g., benzil and its 4,4′-dimethyl and 4,4′-dimethoxy analogues) have been shown to be unresponsive toward methyl viologen.[24]

Experimental Section

The equipment and procedures for steady-state photolysis and determination of melting point and spectra are described in previous publications.[3-13]

Starting Materials. Salicylaldehyde (**1a**), bp 98 °C (25 mm), and *o*-hydroxyacetophenone (**1b**) were obtained as commercial samples and were purified by distillation before use. β-Hydroxy-α-naphthaldehyde (**1c**),[25] mp 82–84 °C, and dibenzoylacetylene (DBA, **2**),[26] mp 110–111 °C, were prepared by reported procedures. Solvents for steady-state photolysis experiments were purified and distilled before use. Aldrich Gold-Label solvents were used for laser studies. Petroleum ether used was the fraction with bp 60–80 °C.

Preparation of 2,3-Dibenzoyl-4*H*-1-benzopyran-4-ol (3a). A mixture of **1a** (122 mg, 1 mmol), **2** (234 mg, 1 mmol), and anhydrous potassium carbonate (138 mg, 1 mmol) in acetone (20 mL) was stirred at room temperature (25 °C) for 3 h, and the inorganic material was removed by filtration. Removal of the solvent under vacuum gave a solid, which on trituration with a small quantity of methanol, followed by recrystallization from a mixture (2:1) of benzene and petroleum ether, gave 250 mg (68%) of **2a**, mp 137–138 °C: IR ν_{max} (KBr) 3445 (OH), 3060, 3045, 2920, and 2885 (CH), 1660 and 1628 (C=O), 1595 and 1585 (C=C) cm^{-1}; UV λ_{max} (methanol) 253 nm (ε 20 000), 279 (9820 sh), and 298 (6400 sh); ^1H NMR ($CDCl_3$) δ 3.60 (1 H, d, *J* = 7 Hz, OH, D_2O-exchangeable), 5.83 (1 H, d, *J* = 7 Hz, methine proton), 7.15–7.76 (14 H, m, Ar); mass spectrum, *m/e* (relative intensity) 356 (M^+, 10), 339 (M^+ – OH, 66), 338 ($M^+ - H_2O$, 85), 311 (10), 277 (21), 251 ($M^+ - COC_6H_5$, 100), 173 (50), 105 ($COC_6H_5^+$, 13), and other peaks.

Anal. Calcd for $C_{23}H_{16}O_4$: C, 77.54; H, 4.49. Found: C, 77.83; H, 4.60.

Preparation of 2,3-Dibenzoyl-4-methyl-4*H*-1-benzopyran-4-ol (3b). A mixture of **1b** (136 mg, 1 mmol), **2** (234 mg, 1 mmol), and anhydrous potassium carbonate (138 mg, 1 mmol) in acetone (20 mL) was stirred at room temperature (25 °C) for 0.5 h. Removal of the inorganic material by filtration, followed

---

[22] Nemoto, M.; Kokubun, H.; Koizumi, M. *Bull. Chem. Soc. Jpn.* **1969**, *42*, 1223–1230.

[23] The bimolecular rate constant for electron transfer from $^{\bullet}CH_2OH$ to PQ^{2+} is 3×10^8 M^{-1} s^{-1} in water containing 3% methanol. See: Patterson, L. K.; Small, R. D. Jr.; Scaiano, J. C. *Radiat. Res.* **1977**, *72*, 218–225.

[24] Rajadurai, S.; Das, P. K., unpublished results.

[25] Russel, A.; Lockhart, L. B. *Organic Syntheses*; Blatt, A. H., Ed.; Wiley: New York, 1955; Collect. Vol. 3, pp 463–464.

[26] (a) Lutz, R. E.; Smithey, W. R. *J. Org. Chem.* **1951**, *16*, 51–56. (b) Lutz, R. E. *Organic Syntheses*; Blatt, A. H., Ed.; Wiley: New York, 1955; Collect. Vol. 3, pp 249–250.

by removal of the solvent under vacuum, gave a viscous liquid, which solidified on treatment with a small amount of methanol. Recrystallization of the resultant solid from a mixture (2:1) of benzene and petroleum ether gave 230 mg (63%) of **3b**, mp 173–174 °C: IR ν_{max} (KBr) 3560 and 3440 (OH), 3060, 2965, and 2920 (CH), 1665 and 1630 (C=O), 1585, 1565, and 1475 (C=C) cm^{-1}; UV λ_{max} (methanol) 253 nm (ϵ 20 500), 290 (7400 sh), and 314 (3540 sh); ^{1}H NMR ($CDCl_3$) δ 1.80 (3 H, s, methyl), 3.92 (1 H, s, OH, D_2O-exchangeable), and 6.75–8.18 (14 H, m, Ar); mass spectrum, *m/e* (relative intensity) 370 (M^+, 2), 355 ($M^+ - CH_3$, 100), 354 (8), 352 ($M^+ - H_2O$, 34), 277 (74), 247 ($M^+ - H_2O - COC_6H_5$, 8), 219 (9), 105 ($COC_6H_5^+$, 19), and other peaks.

Anal. Calcd for $C_{24}H_{18}O_4$: C, 77.84; H, 4.86. Found: C, 78.14; H, 4.73.

In a repeat run, treatment of **1b** with **2** in presence of potassium carbonate in THF for 1 h at room temperature gave a 73% yield of **3b**.

Preparation of 2,3-Dibenzoyl-1*H*-naphtho[2,1-*b*]pyran-1-ol (3c). A mixture of **1c** (0.74 g, 4.3 mmol), **2** (1.0 g, 4.3 mmol), and anhydrous potassium carbonate (0.59 g, 4.3 mmol) in acetone (10 mL) was stirred at room temperature (25 °C) for 0.5 h, and the inorganic material was removed by filtration. Removal of the solvent under vacuum gave a solid, which was recrystallized from a mixture (1:2) of benzene and petroleum ether to give 1.5 g (86%) of **3c**, mp 165–166 °C: IR ν_{max} (KBr) 3510 and 3440 (OH), 3050 and 3020 (CH), 1665 and 1630 (C=O), 1610 and 1590 (C=C) cm^{-1}; UV λ_{max} (methanol) 234 nm (ϵ 40 800), 259 (25 500, sh), 271 (21 500 sh), 281 (16 600 sh), 311 (3500 sh), and 325 (2600 sh); ^{1}H NMR ($CDCl_3$) δ 3.37 (1 H, d, *J* = 6 Hz, OH, D_2O-exchangeable), 6.60 (1 H, d, *J* = 6 Hz, methine proton), 6.78–8.03 (16 H, m, Ar); mass spectrum, *m/e* (relative intensity) 406 (M^+, 2), 389 (10), 388 ($M^+ - H_2O$, 10), 301 ($M^+ - COC_6H_5$, 78), 300 (65), 224 ($M^+ - COC_6H_5 - C_6H_5$, 47), 105 ($COC_6H_5^+$, 100), and other peaks.

Anal. Calcd for $C_{27}H_{18}O_4$: C, 79.80; H, 4.43. Found: C, 79.56; H, 4.68.

Preparation of 2,3-Dibenzoyl-2*H*-1-benzopyran-2-ol (4a). A mixture of **1a** (122 mg, 1 mmol), **2** (234 mg, 1 mmol), and anhydrous potassium carbonate (138 mg, 1 mmol) was stirred in refluxing acetone (20 mL) for 4 h. Subsequent workup as in the earlier cases gave 200 mg (58%) of **4a**, mp 170–171 °C, on recrystallization from a mixture (3:1) of benzene and petroleum ether: IR ν_{max} (KBr) 3434 (OH), 3045, 2920 (CH), 1694, 1634 (C=O), 1610, 1570 (C=C) cm^{-1}; UV λ_{max} (methanol) 245 nm (ϵ 23 600), 300 (14 400), and 345 (7400); ^{1}H NMR ($CDCl_3$) δ 6.18 (1 H, s, OH, D_2O-exchangeable), 7.05–8.15 (15 H, m, Ar and vinylic); mass spectrum, *m/e* (relative intensity) 356 (M^+, 1), 339 ($M^+ - OH$, 9), 311 (3), 251 ($M^+ - COC_6H_5$, 78), 174 ($M^+ - COC_6H_5 - C_6H_5$, 58), 173 ($M^+ - COC_6H_5 - H$, 100), 145 (13), 105 ($COC_6H_5^+$, 12), and other peaks.

Anal. Calcd for $C_{23}H_{16}O_4$: C, 77.54; H, 4.49. Found: C, 77.67; H, 4.27.

Preparation of 2,3-Dibenzoyl-4*H*-1-benzopyran-4-one (6a). A mixture of **3a** (1.0 g, 2.8 mmol) and freshly prepared nickel peroxide[27] (1.0 g, 11.1 mmol) was stirred in benzene (20 mL) for 40 h at room temperature (25 °C). Removal of the inorganic material and the solvent gave a solid, which was recrystallized from a mixture (1:1) of benzene and petroleum ether to give 0.95 g (96%) of **6a**, mp 150–151 °C (lit.[28] mp 149–150 °C): IR ν_{max} (KBr) 3060 and 3015 (CH), 1673, 1638, and 1615 (C=O), 1594 and 1565 (C=C) cm^{-1}; UV λ_{max} (methanol) 248 nm (ϵ 23 900), and 305 (7790 sh); ^{1}H NMR ($CDCl_3$) δ 7.08–8.25 (m, Ar); mass spectrum, *m/e* (relative intensity) 354 (M^+, 80), 326 ($M^+ - CO$, 17), 298 ($M^+ - 2CO$, 10), 279 ($M^+ - C_6H_5$, 10), 278 (54), 249 ($M^+ - COC_6H_5$, 26), 105 ($COC_6H_5^+$, 98), 77 ($C_6H_5^+$, 100), and other peaks.

Anal. Calcd for $C_{23}H_{14}O_4$: C, 77.96; H, 3.95. Found: C, 77.73; H, 4.12.

Irradiation of 3a. A solution of **3a** (500 mg, 1.4 mmol) in benzene (350 mL) was irradiated for 8 h (RPR, 3000 Å) at room temperature (25 °C). The color of the solution became blue initially, which turned dark yellow on prolonged irradiation. Removal of the solvent under vacuum gave a residue, which was chromatographed over silica gel. Elution with a mixture (1:9) of ethyl acetate and benzene gave 305 mg (61%) of **4a**, mp 171–172 °C (mixture mp). In a blank run, a solution of **3a** (100 mg, 0.28 mmol) in dry benzene (10 mL) was refluxed for 10 h. Removal of the solvent under vacuum and recrystallization of the residual solid from a mixture (2:1) of benzene and petroleum ether gave the unchanged starting material (**3a**, 90 mg, 90%), mp 137–138 °C (mixture mp).

In a repeat run, **3a** was photolyzed in acetone under analogous conditions to give a 74% yield of **4a**.

Irradiation of **3a** (500 mg, 1.4 mmol) in methanol (350 mL), under analogous conditions for 8 h, followed by removal of the solvent under vacuum gave a solid, which was chromatographed over silica gel. Elution with petroleum ether gave 52 mg (10%) of 2,3-dibenzoyl-2-methoxy-2*H*-1-benzopyran (**8a**), mp 110–111 °C, after recrystallization from methanol: IR ν_{max} (KBr) 3050, 2970, and 2825 (CH), 1700 and 1650 (C=O), 1630, 1600, and 1570 (C=C) cm^{-1}; UV λ_{max} (methanol) 245 nm (ϵ 38 200), 295 (25 600), 340 (11 400); ^{1}H NMR ($CDCl_3$) δ 3.54 (3 H, s, methoxy), 7.15–8.20 (15 H, m, Ar and vinylic).

Anal. Calcd for $C_{24}H_{18}O_4$: C, 77.84; H, 4.86. Found: C, 77.61; H, 4.97.

Subsequent elution of the column with the same mixture (1:9) of ethyl acetate and benzene gave 260 mg (52%) of **4a**, mp 171–172 °C (mixture mp).

Acid-Catalyzed Conversion of 3a to 4a. A solution of **2a** (90 mg, 0.25 mmol) in methanol (10 mL), containing a small amount hydrochloric acid (1 mL of 0.1 N HCl) was refluxed for 10 min. Removal of the solvent under vacuum gave 70 mg (77%) of **4a**, mp 170–171 °C (mixture mp), after recrystallization from a mixture (3:1) of benzene and petroleum ether.

Acid-Catalyzed Conversion of 3a to 8a. A solution of **3a** (356 mg, 1 mmol) in dry methanol (10 mL) was refluxed with *p*-toluenesulfonic acid (5 mL of 0.1 N acid) for 1 h. The reaction mixture was cooled and then neutralized with pyridine. Removal of the solvent under vacuum gave a residual solid, which was extracted with ether. The ether extract was washed with water and dried over anhydrous sodium sulfate, and the solvent was removed under vacuum to give 100 mg (28%) of **8a**, mp 110–111 °C (mixture mp), after recrystallization from methanol.

Irradiation of 3b. A solution of **3b** (500 mg, 1.35 mmol) in benzene (350 mL) was irradiated (RPR, 2537 Å) for 3 h. Removal of the solvent under vacuum gave a solid, which was chromatographed on silica gel. Elution with a mixture (1:1) of ethyl acetate and benzene gave 300 mg (63%) of **5b**, mp 220–221 °C, after recrystallization from a mixture (1:1) of acetone and petroleum ether: IR ν_{max} (KBr) 3045 and 2940 (CH), 1670 and 1635 (C=O), 1580 and 1570 (C=C) cm^{-1}; UV λ_{max} (tetrahydrofuran) 257 nm (ϵ 25 400), and 314 (3560 sh); ^{1}H NMR ($CDCl_3$) δ 4.81 (1 H, s, methylene), 5.56 (1 H, s, methylene), 7.15–8.21 (14 H, m, Ar); mass spectrum, *m/e* (relative intensity) 352 (M^+, 26), 323 (10), 298 (6), 247 ($M^+ - COC_6H_5$, 5), 219 (10), 105 ($COC_6H_5^+$, 62), and other peaks.

Anal. Calcd for $C_{24}H_{16}O_3$: C, 81.81; H, 4.54. Found: C, 81.57; H, 4.78.

In repeat runs, **3b** was photolyzed under analogous conditions in acetone and methanol to give **5b** in 55% and 62% yields, respectively.

Acid-Catalyzed Conversion of 3b to 5b. A solution of **3b** (200 mg, 0.54 mmol) in methanol (10 mL), containing 0.1 N hydrochloric acid (5 mL) was refluxed for 5 min. The mixture, on cooling, was neutralized with pyridine and, after removal of the solvent under vacuum, gave a viscous material, which was chromatographed over silica gel. Elution with a mixture (1:1) of ethyl acetate and benzene gave 115 mg (60%) of **5b**, mp 220–221 °C (mixture mp).

Conversion of 3b to 8b. To a solution of **3b** (200 mg, 0.54 mmol) in methanol (10 mL) was added 2 mL of 0.1 N *p*-toluenesulfonic acid at 10 °C, and the mixture was stirred at 15–20 °C for 1 h. The solid that separated out on cooling was recrystallized from methanol to give 90 mg (44%) of **8b**, mp 108–109 °C: IR ν_{max} (KBr) 3040, 3005, 2920, and 2820 (CH), 1675 (C=O), 1590 and 1520 (C=C) cm^{-1}; UV λ_{max} (methanol) 216 nm (ϵ 35 000),

---

[27] (a) Nakagawa, K.; Konaka, R.; Nakata, T. *J. Org. Chem.* **1962**, *27*, 1597–1601. (b) George, M. V. *Organic Synthesis by Oxidation with Metal Compounds*; Mijs, W. J., de Jonge, C. R. H, I., Eds.; Plenum: New York, 1986; pp 373–422.

[28] Henderson, W. A., Jr.; Ullman, E. F. *J. Am. Chem. Soc.* **1965**, *87*, 5424–5433.

260 (15 000), 270 (14 000), and 302 (5500); ^{1}H NMR (CDCl$_3$) δ 2.40 (3 H, s, methyl), 3.49 (3 H, s, methoxy), 7.05–8.00 (14 H, m, Ar).

Anal. Calcd for $C_{25}H_{20}O_4$: C, 78.12; H, 5.20. Found: C, 77.85; H, 4.98.

Irradiation of 3c. A solution of **3c** (500 mg, 1.23 mmol) in benzene (350 mL) was irradiated (RPR, 2537 Å) for 8 h at room temperature (25 °C). Removal of the solvent under vacuum gave a solid, which was chromatographed over silica gel. Elution with a mixture (1:1) of benzene and petroleum ether gave 100 mg (20%) of **9c**, mp 209–210 °C, after recrystallization from a mixture (1:9) of benzene and petroleum ether: IR ν_{max} (KBr) 3040 and 2980 (CH), 1700, 1650, and 1640 (C=O), 1590 (C=C) cm^{-1}; UV λ_{max} (methanol) 226 nm (ϵ 69 000 sh), 230 (69 000 sh), 256 (25 000), 328 (11 000), and 369 (17 000); ^{1}H NMR (CDCl$_3$) δ 7.17–8.38 (17 H, m, Ar and vinylic), 8.94 (1 H, s, aldehydic); mass spectrum, *m/e* (relative intensity) 406 (M$^+$, 0.3), 301 (M$^+$ – COC$_6$H$_5$, 3), 300 (M$^+$ – COC$_6$H$_5$ – H, 69), 299 (9), 105 (COC$_6$H$_5$$^+$, 100), 77 (C$_6H_5$$^+$, 88), and other peaks.

Anal. Calcd for $C_{27}H_{18}O_4$: C, 79.80; H, 4.43. Found: C, 79.62; H, 4.71.

Further elution of the column with benzene gave 220 mg (44%) of **4c**, mp 195–196 C, after recrystallization from a mixture (1:1) of benzene and petroleum ether: IR ν_{max} (KBr) 3360 (OH), 3060, 3045, and 3020 (CH), 1683 and 1660 (C=O), 1610 and 1590 cm^{-1}; UV λ_{max} (methanol) 230 nm (ϵ 46 200), 252 (25 100 sh), 322 (7600 sh), 335 (8760), and 384 (11 500); ^{1}H NMR (CDCl$_3$) δ 6.15 (1 H, s, OH, D$_2$O-exchangeable), 7.05–8.25 (17 H, m, Ar and vinylic); mass spectrum, *m/e* (relative intensity) 406 (M$^+$, 2), 389 (M$^+$ – OH, 2), 388 (M$^+$ – H$_2$O, 2), 301 M$^+$ – COC$_6$H$_5$, 80), 224 (M$^+$ – COC$_6$H$_5$, 62), 105 (COC$_6$H$_5$$^+$, 66), 77 (C$_6H_5$$^+$, 100), and other peaks.

Anal. Calcd for $C_{27}H_{18}O_4$: C, 79.80; H, 4.43. Found: C, 79.56; H, 4.59.

In a repeat run, **3c** was photolyzed in acetone for 4 h, under analogous conditions, to give a 85% yield of **4c**.

In another run, a solution of **3c** (500 mg, 1.23 mmol) in methanol (350 mL) was irradiated (RPR, 2537 Å) for 6 h, and the solvent was removed under vacuum to give a solid, which was chromatographed over silica gel. Elution with a mixture (1:1) of benzene and petroleum ether gave 135 mg (26%) of **8c**, mp 125–126 °C, after recrystallization from a mixture (1:2) of benzene and petroleum ether: IR ν_{max} (KBr) 3045, 3020, 2945, 2915, and 2840 (CH), 1700 and 1630 (C=O), 1620, 1590, and 1570 (C=C) cm^{-1}; UV λ_{max} (methanol) 230 nm (ϵ 48 300), 254 (28 000), 334 (9270), and 381 (11 800); ^{1}H NMR (CDCl$_3$) δ 3.58 (3 H, s, methoxy), 7.28–8.30 (17 H, m, Ar and vinylic).

Anal. Calcd for $C_{28}H_{20}O_4$: C, 80.00; H, 4.76. Found: C, 79.74; H, 4.68.

Further elution with benzene gave 200 mg (40%) of **4c**, mp 195–196 °C (mixture mp), after recrystallization from a mixture (1:2) of benzene and petroleum ether.

In a blank run, a solution of **3c** (100 mg, 0.246 mmol) in methanol (15 mL) was refluxed for 8 h and worked up in the usual manner to give a 90% recovery (90 mg) of the unchanged starting material (**3c**), mp 165–166 °C (mixture mp).

Acid-Catalyzed Conversion of 3c to 4c. A solution of **3c** (100 mg, 0.25 mmol) in methanol (10 mL), containing 0.1 N hydrochloric acid (5 mL), was refluxed for 1 h. Removal of the solvent under vacuum gave a solid, which was washed with ether and chromatographed over silica gel. Elution with benzene gave 52 mg (52%) of **4c**, mp 195–196 °C (mixture mp).

Acid-Catalyzed Conversion of 3c to 8c. To a solution of **3c** (500 mg, 1.23 mmol) in dry methanol (20 mL) was added 5 mL of 0.1 N *p*-toluenesulfonic acid and the mixture refluxed for 4 h. On cooling, the reaction mixture was neutralized with pyridine and the solvent removed under vacuum to give a product, which was extracted with ether. Removal of the solvent from the ether extract gave a solid, which was chromatographed over silica gel. Elution with petroleum ether gave 295 mg (57%) of **8c**, mp 125–126 °C (mixture mp), after recrystallization from a mixture (1:2) of benzene and petroleum ether.

Irradiation of 4a. A solution of **4a** (500 mg, 1.4 mmol) in dry methanol (350 mL) was irradiated (RPR, 2537 Å) for 15 h. Removal of the solvent under vacuum gave a solid, which was chromatographed over silica gel. Elution with a mixture (1:1) of benzene and petroleum ether gave 185 mg (36%) of **8a**, mp 110–111 °C (mixture mp).

Further elution of the column with a mixture (1:9) of ethyl acetate and benzene gave 150 mg (30%) of the unchanged starting material (**4a**), mp 171–172 °C (mixture mp).

In a blank run, a solution of **4a** (100 mg, 0.28 mmol) in methanol (20 mL) was refluxed for 15 h and worked up in the usual manner to give the unchanged starting material (**4a**, 90 mg, 90%), mp 171–172 °C.

Acid-Catalyzed Conversion of 4a to 8a. A solution of **4a** (356 mg, 1 mmol) in dry methanol (10 mL), containing a small amount of 98% sulfuric acid was refluxed for 20 h. The reaction mixture was cooled and neutralized with pyridine. Removal of the solvent under vacuum gave a product mixture, which was extracted with ether. The ether extract was washed with water, dried over anhydrous sodium sulfate, and, after removal of the solvent under vacuum, gave 150 mg (44%) of **8a**, mp 110–111 °C (mixture mp), after recrystallization from methanol.

Attempted Photolysis of 2,3-Dibenzoyl-4-methylene-4*H*-1-benzopyran (5b). A solution of **5b** (250 mg, 0.71 mmol) in dry benzene (300 mL) was irradiated (RPR 2537 Å) for 25 h. Removal of the solvent under vacuum gave a residual solid, which was chromatographed over silica gel. Elution with a mixture (1:9) of ethyl acetate and benzene gave 210 mg (84%) of the unchanged starting material, mp 220–221 °C (mixture mp).

In a repeat run, **5b** (1.0 g, 2.84 mmol) was irradiated (Hanovia 450-W, medium-pressure mercury lamp in a quartz-jacketed immersion well) in a mixture (9:1) of benzene and methanol for 15 h. Removal of the solvent under vacuum and chromatographing the residue over silica gel (elution with a mixture (1:9) of ethyl acetate and benzene) gave the unchanged starting material (**5b**, 650 mg, 65%), mp 220–221 °C (mixture mp), as the only isolable product.

Attempted Photolysis of 2,3-Dibenzoyl-4*H*-1-benzopyran-4-one (6a). A solution of **6a** (500 mg, 1.4 mmol) in dry benzene (500 mL) was irradiated (RPR 2537 Å) for 26 h. Removal of the solvent under vacuum gave a solid, which was chromatographed over silica gel. Elution with a mixture (1:1) of benzene and petroleum ether gave 300 mg (60%) of the unchanged starting material (**6a**), mp 150–151 °C (mixture mp).

In a repeat run, a solution of **6a** (500 mg, 1.4 mmol) in a mixture (2:1) of benzene and methanol (500 mL) was irradiated for 30 h under the same light source and worked up as in the earlier case to give a 65% recovery (325 mg) of the unchanged starting material (**6a**), mp 151–152 °C (mixture mp).

Laser Flash Photolysis. The laser pulse excitation was usually carried out at 337.1 nm (2–3 mJ, ~8 ns), employing a UV 400 Molectron nitrogen laser. For some experiments, use was also made of laser pulses at 355, 485, and 532 nm (Quanta-Ray DCR-1 Nd:YAG coupled with PDL-1 dye laser, 6 ns, ≤50 mJ) as well as at 308 nm (Lambda-Physik EMG MSC gas excimer, 20 ns, ≤50 mJ). Descriptions of the setup and procedures are given elsewhere.[29]

Acknowledgment. We thank the Department of Science and Technology, Government of India, Indian Institute of Technology, and Kanpur, and the Office of Basic Energy Sciences of the U.S. Department of Energy for financial support of this work. We gratefully acknowledge the interest and participation of Dr. S. Rajadurai in some of the preliminary laser flash photolysis experiments.

---

[29] (a) Das, P. K.; Encinas, M. V.; Small, R. D., Jr.; Scaiano, J. C. *J. Am. Chem. Soc.* **1979**, *101*, 6965–6970. (b) Das, P. K.; Bobrowski, K. *J. Chem. Soc., Faraday Trans. 2*, **1981**, *77*, 1009–1027. (c) Chattopadhyay, S. K.; Das, P. K.; Hug, G. *J. Am. Chem. Soc.* **1982**, *104*, 4507–4514.