4.50 (s, 2 H), 4.20 (br, 1 H), 2.22 (s, 6 H).[33]

General Procedure for *tert*-Butylation of Heterocyclic Aromatic Substances (Table V). To a mixture of thiophene (336 mg, 4 mmol), SiO_2 (1 g), and Na_2CO_3 (1.272 g, 12 mmol) in CCl_4 (4 mL) was added 12 mmol (1.644 g) of *t*-BuBr. The mixture was stirred for 40 h at 78 °C. The reactions of 2-methylthiophene, benzothiophene, and 1-methylindol were carried out quite similarly. The furan reaction was carried out at 25 °C for 24 h and then at 78 °C for another 24 h. In each case SiO_2 was filtered off and washed with CH_2Cl_2 thoroughly. The washings were combined with the filtrate and the solvent was removed. Crude materials were analyzed by GC and ^1H NMR. Purification for microanalyses by ball tube distillation afforded **26** (768 mg, 98%), **27** (376 mg, 61%), **28** (734 mg, 51%), **29** (539 mg, 78%), and **30** (374 mg, 50%). The data for **26–30** follow. **26**: bp 120 °C (20 torr); ^1H NMR ($CDCl_3$) δ 6.45 (s, 2 H), 1.30 (s, 18 H).[34] **27**: bp 160 °C (20 torr); ^1H NMR ($CDCl_3$) δ 6.50 (s, 2 H), 2.42 (s, 3 H), 1.32 (s, 9 H).[35] **28**: bp 80 °C (12 torr); ^1H NMR ($CDCl_3$) δ 5.77 (s, 2 H), 1.23 (s, 18 H).[36] **29**: bp 150 °C (6 torr); ^1H NMR ($CDCl_3$) δ 7.15–8.16 (m, 4 H), 7.06 (s, 1 H), 1.43 (s, 9 H).[37] **30**: bp 170 °C (0.1 torr); ^1H NMR ($CDCl_3$) δ 6.83–7.90 (m, 4 H), 6.54 (s, 1 H), 3.60 (s, 3 H), 1.40 (s, 9 H).[38]

Registry No. **1**, 88-18-6; **2**, 98-54-4; **3**, 96-76-4; **4**, 128-39-2; **5**, 732-26-3; **6**, 120-80-9; **7**, 108-46-3; **8**, 123-31-9; **9**, 92-88-6; **10**, 135-19-3; **11**, 100-66-3; **12a**, 4026-05-5; **12b**, 98-29-3; **12c**, 1020-31-1; **13a**, 2206-50-0; **13b**, 5374-06-1; **14a**, 1948-33-0; **14b**, 88-58-4; **15a**, 91798-62-8; **15b**, 60803-40-9; **15c**, 61514-62-3; **15d**, 128-38-1; **16**, 1081-32-9; **17a**, 2944-48-1; **17b**, 5396-38-3; **18a**, 576-26-1; **19**, 879-97-0; **20**, 91798-63-9; **21**, 55563-86-5; **22**, 91798-64-0; **23**, 21104-18-7; **24a**, 5384-21-4; **24b**, 118-82-1; **24c**, 107-30-2; **25**, 28193-66-0; **26**, 4789-40-6; **27**, 15146-95-9; **28**, 1689-77-6; **29**, 35181-78-3; **30**, 46270-99-9; C_6H_5OH, 108-95-2; SiO_2, 7631-86-9; Al_2O_3, 1344-28-1; *t*-BuBr, 507-19-7; $C_2H_5(CH_3)_2CBr$, 507-36-8; *p*-$TolCH_2Cl$, 104-82-5; $CH_2{=}CHCH(CH_3)Cl$, 563-52-0; thiophene, 110-02-1; 2-methylthiophene, 554-14-3; furan, 110-00-9; benzothiophene, 95-15-8; 1-methylindole, 603-76-9.

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Photochemical Transformations and Laser Flash Photolysis Studies of 1,4- and 1,2-Epoxy Compounds Containing 1,2-Dibenzoylalkene Moieties[1]

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Photochemical transformations of a few 1,4- and 1,2-epoxy ketones have been investigated. Irradiation of a benzene solution of **1** gave a mixture of **3** (32%) and dibenzoylacetylene (DBA, **6**, 13%), whereas the photolysis of **8** in methanol gave a mixture of the ester **12** (56%) and DBA (22%). Irradiation of **14** in benzene gave a mixture of the isomeric lactone **17** (25%), 1,3-diphenylisobenzofuran (**20**, 20%), and *o*-dibenzoylbenzene (**23**, 10%). The photolysis of **24** in both benzene and methanol resulted in isomerization to the anthracene derivative **25** (6% and 20%). The same product (**25**, 38%) was obtained in the thermolysis of **24**. Plausible mechanisms for the formation of the various products have been discussed. Laser flash photolysis (337.1 nm) of **1**, **8**, and **14** in benzene and methanol led to the observation of short-lived transient species, characterized by absorption maxima at 405–490 nm and by lifetimes (τ_T) in the range 0.4–2.0 μs. Pulse-radiolytic observation of the same transients under energy-transfer sensitization as well as detailed quenching studies using oxygen, di-*tert*-butylnitroxide, azulene, ferrocene, and β-carotene led to the assignments of the transients as triplets. The quantum yields of triplet formation (Φ_T) under direct laser excitation were estimated to be high (0.50–0.74). Upon laser flash photolysis, **24** produced the anthracene derivative **25** nearly within the laser pulse; the intermediacy of a triplet with $\tau_T \sim 7$ ns and $\Phi_T \sim 1$ was established in this case by quenching studies involving 1-methylnaphthalene and 2,5-dimethyl-2,4-hexadiene.

Introduction

Phototransformations of several 1,4-epoxy compounds containing ester substituents have been reported earlier.[3-8] Thus, 7-oxanorbornadienes on direct irradiation give oxaquadricyclanes, presumably through a $[\pi^2s + \pi^2s]$ addition. In contrast, the sensitized irradiations of oxaquadricyclanes lead to 6-hydroxyfulvenes. Similarly, direct irradiation of benzoxanorbornadienes gives benzoxepine derivatives,[9-11] whereas, indene derivatives have been isolated in the sensitized irradiation of certain benzoxanorbornadienes.[11]

Photochemical transformations of several 1,2-epoxy compounds containing carbonyl substituents have been investigated in detail.[12-16] An interesting case is that of

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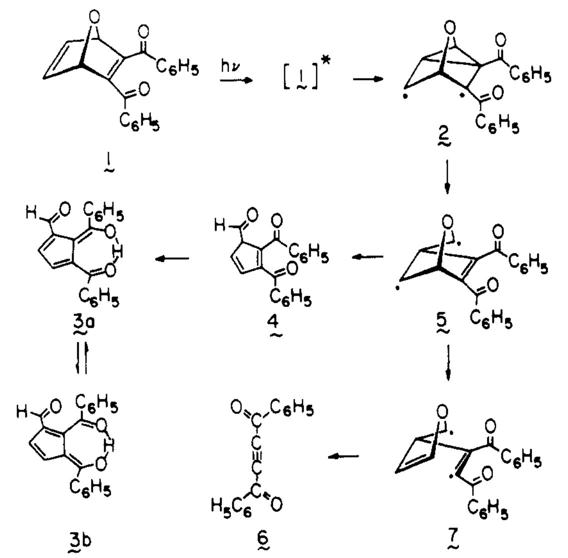
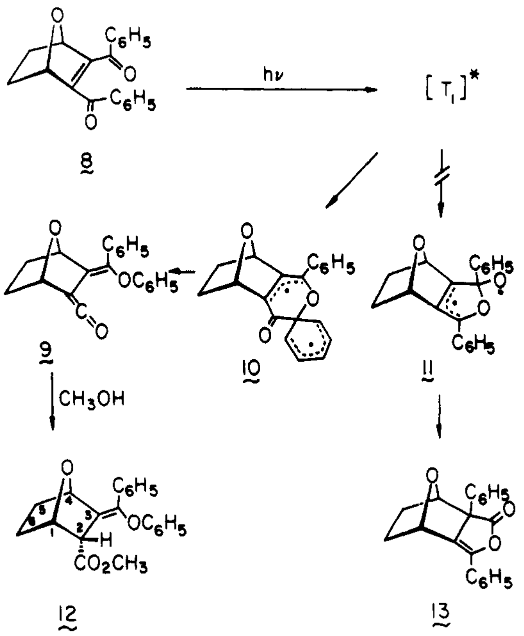
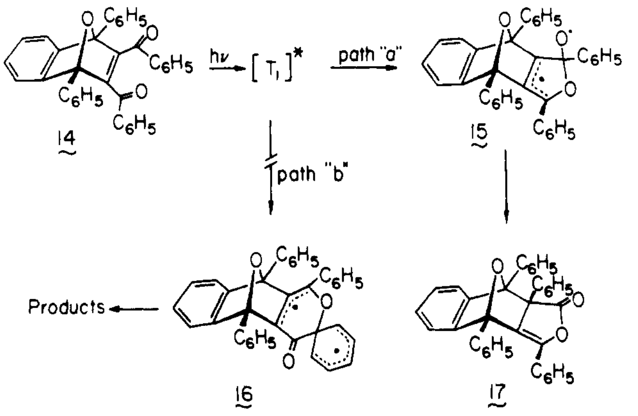
Scheme I



Scheme II



Scheme III



7-benzoyl-7,8-epoxydibenzobicyclo[2.2.2]octa-2,5-diene which, on irradiation, gives an anthracene derivative.[12]

In the present studies, we have examined the steady-state photoreactions of some 1,4- and 1,2-epoxy compounds, containing 1,2-dibenzoylalkene or alkane moieties to investigate the nature of the products formed in these cases. Also, flash photolysis studies have been carried out to characterize the transients in these photoreactions. The photoreactions of these substrates can, in principle, proceed through two distinct pathways—one involving the reaction of the 1,4- or 1,2-epoxy component and the other, related to the rearrangement of the 1,2-dibenzoylalkene fragment. 1,2-Dibenzoylalkenes are known to undergo photorearrangements, giving rise to different products, namely esters and acids, depending on the reaction conditions.[17-25] Thus, the irradiation of 2,3-dibenzoylbicyclo[2.2.2]octa-2,5-diene in methanol gives a mixture of isomeric esters methyl 6-(phenoxyphenylmethylene)bicyclo[2.2.2]oct-2-ene-5-*exo*-carboxylate and methyl 6-(phenoxyphenylmethylene)bicyclo[2.2.2]oct-2-ene-5-*endo*-carboxylate, whereas in benzene, a mixture of the corresponding carboxylic acids and a lactone is formed.[22]

The substrates that we have examined in the present studies include 7-oxa-2,3-dibenzoylbicyclo[2.2.1]hepta-2,5-diene (**1**), 7-oxa-2,3-dibenzoylbicyclo[2.2.1]hept-2-ene (**8**), 1,4-diphenyl-2,3-dibenzoyl-1,4-epoxy-1,4-dihydronaphthalene (**14**), and 9,10-dihydro-9,10-(1,2-dibenzoyl-1,2-epoxyethano)anthracene (**24**).

Results and Discussion

(1) Preparative Photochemistry and Product Identification. Irradiation of a benzene solution of **1** gave a mixture of 1-benzoyl-4-formyl-5-(hydroxyphenylmethylene)-1,3-cyclopentadiene (**3**, 32%) and dibenzoylacetylene (DBA, **6**, 13%) (Scheme I). The structure of **3** was established on the basis of analytical results and spectral data. It may be pointed out that the hydroxyfulvene **3** could exist as a mixture of two possible tautomeric forms **3a** and **3b** in solution and the existence of such tautomeric mixtures has been reported earlier.

The formation of **3** and DBA from **1** may be explained in terms of the pathway shown in Scheme I. It is pertinent to note that unlike in the direct irradiation of oxanorbornadienes, leading to oxaquadricyclanes and products derived from them, the direct irradiation of **1** leads to the rearrangement product **3**, which could arise directly from the singlet excited state or through the triplet state, involving diradical intermediates **2**, **5**, and **7** (Scheme I).

Unlike **1**, the direct irradiation of **8** in methanol gave a mixture of methyl 3-(phenoxyphenylmethylene)-7-oxabicyclo[2.2.1]heptane-2-carboxylate (**12**, 56%) and DBA (22%). The structure of **12** was established on the basis of analytical data and spectral evidence. The formation of **12** from **8** may proceed through the pathway shown in Scheme II, involving the ketene intermediate **9**. The formation of DBA, however, could be due to the photofragmentation of **8**.

Irradiation of a benzene solution of **14** gave a mixture of the lactone **17** (25%), 1,3-diphenylisobenzofuran (**20**, 20%), and *o*-dibenzoylbenzene (**23**, 10%). The formation of **17** could be explained in terms of path "a" shown in

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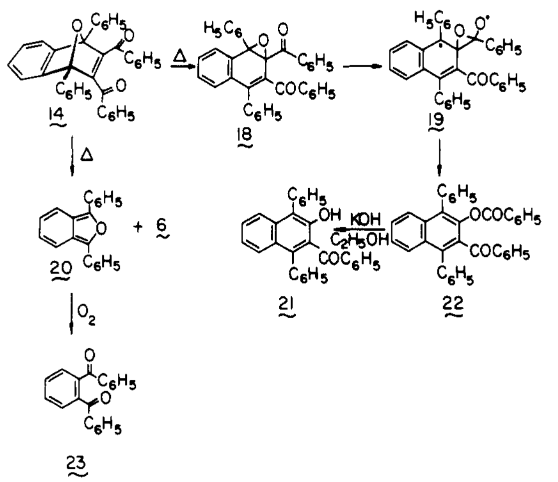
Table I. Spectral and Kinetic Data Concerning the Triplets of 1,4- and 1,2-Epoxy Compounds under Study

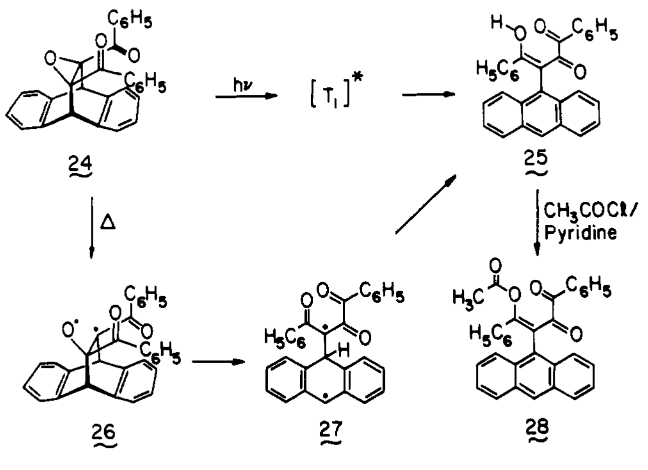
no.	solvent	k_q^T,[a] 10^9 M^{-1} s^{-1}	Φ_T[b]	λ_{max},[c] nm	ϵ_T,[b] 10^3 M^{-1} cm^{-1}	τ_T,[d] μs	k_q^T,[e] 10^9 M^{-1} s^{-1} O_2	DTBN	azulene	ferrocene	β-carotene
1	benzene	2.4	0.70	410	5.64	0.45	1.38	0.88	1.1	8.4	5.4
	methanol		0.65	405		0.41	1.50				
8	benzene	4.5	0.74	~450[f]	2.70	1.4	0.46	1.53	1.6	10.8	5.5
	methanol		0.51	~420[f]		1.2	0.40				
14	benzene	2.8	0.66	490	5.27	1.7	0.50	0.97	1.9	9.0	4.5
	methanol		0.50	480		1.6	0.40				
24	benzene	2.7	1.0			0.007					
	methanol										

[a] Rate constant for the quenching of *p*-methoxyacetophenone triplet by the substrates ±15%. [b] ±25%. [c] ±5 nm. [d] ±15%. [e] Rate constants for the quenching of substrate triplets. [f] Based on the shoulder at 400–500 nm.

Scheme IV



Scheme V



Scheme III. It is interesting to note that none of the rearrangement products arising through path "b", involving the intermediate **16**, could be isolated. One of the contributing factors for the product selectivity in the photolysis of **14** could be the ground-state conformational preferences of this compound, containing two bulky phenyl substituents at the bridgehead positions. The formation of 1,3-diphenylisobenzofuran (**20**), however, could occur through a retro-Diels–Alder fragmentation of **14**, whereas *o*-dibenzoylbenzene may arise through the air oxidation of **20**.[26]

In contrast to the photoreaction, the thermal reaction of **14** follows an entirely different pathway. Heating of **14** at ca. 320 °C gave a mixture of 3-benzoyl-2-(benzoyloxy)-1,4-diphenylnaphthalene (**22**, 16%), **20** (10%), and **23** (4%). The structure of **22** was arrived at on the basis of analytical results, spectral data, and chemical evidence. Refluxing a mixture of **22** with ethanolic potassium hydroxide gave 3-benzoyl-1,4-diphenyl-2-naphthol (**21**, 33%), which could be reconverted to **22**, on treatment with benzoyl chloride and pyridine. The formation of **22** from **14** may be explained in terms of the pathway shown in Scheme IV.

Irradiation of a benzene solution of the 1,2-epoxy compound **24** for 10 min gave a 6% yield of 2-(9-anthracenyl)-1,4-diphenyl-1-hydroxybut-1-ene-3,4-dione (**25**), whereas the irradiation in methanol for 30 min gave a 20% yield of **25**, besides the recovery of 50% of the starting material (**24**). The structure of **25** was confirmed through its conversion to the acetyl derivative **28** (71%), by treatment with a mixture of acetyl chloride and pyridine.

The thermal reaction of **24** also gave **25**. Thus, neat heating of **24** at ca. 235 °C for 10 min gave a 38% yield of **25**. The photoreaction of **24** may involve its triplet excited state, whereas the thermal transformation may involve diradical intermediates **26** and **27**, as shown in Scheme V.

(2) Laser Flash Photolysis and Pulse Radiolysis Studies. In order to examine the photoinduced transient phenomena on a nano- to microsecond time scale, epoxides **1**, **8**, **14**, and **24** were subjected to laser flash photolysis using nitrogen laser pulses (337.1 nm, ~8 ns, 2–3 mJ) and the spectral absorptions due to the transients were monitored at 300–700 nm.

To sort out triplet-derived transient phenomena, pulse radiolysis[27] in benzene was utilized; in these experiments the solvent triplet (E_T = 84 kcal/mol) transferred its energy to a sensitizer (acetophenone (E_T = 74 kcal/mol) for **24** and biphenyl (E_T = 60 kcal/mol) for other epoxides) present at relatively high concentration (0.05 M). The substrates present at lower concentrations (1–3 mM) quenched the sensitizer triplets giving rise to their own triplets, or triplet-derived products. A flow system was used in all of the experiments based on pulse radiolysis. It may be mentioned that some triplet-sensitization experiments were also carried out by laser flash photolysis by using *p*-methoxyacetophenone (PMA) as the sensitizer (E_T = 72 kcal/mol); in these experiments PMA (0.05–0.1 M) absorbed 50–80% of the exciting laser photons. In benzene, the PMA triplet was quenched by the epoxides with rate constants in the range 2–5 × 10^9 M^{-1} s^{-1} (Table I). The latter data were obtained from the observed pseudo-first-order rate constants for the decay of PMA triplet (monitored by its spectral absorption at 385 nm) as functions of substrate concentrations (0–3 mM). In-

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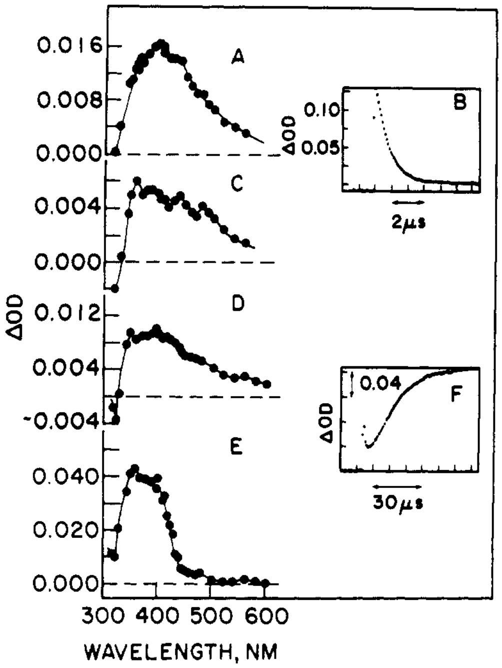

Figure 1. Transient absorption spectra and kinetic traces of 1: (A) T-T absorption spectrum of 1 in methanol; (B) a kinetic trace at 405 nm in methanol; (C) long-lived transient absorption spectrum in methanol; (D and E) absorption spectra of a photoproduct at the onset and completion of growth in methanol; (F) a kinetic trace of the photoproduct in methanol at 390 nm.

terestingly, the quenching of PMA triplet by epoxide **24** forms a case of quasi-isoenergetic[28] (or slightly endothermic) excitation transfer; the observed high rate constant of 2.7×10^9 M^{-1} s^{-1} (Table I) appears to be associated with the fact that the back energy transfer is kinetically unimportant because of the short-lived nature of the triplet of **24** (see later).

(a) 7-Oxa-2,3-dibenzoylbicyclo[2.2.1]hepta-2,5-diene (1). Upon laser flash photolysis in both benzene and methanol, 1,4-epoxide **1** produces a short-lived transient that decays with first-order kinetics ($\tau \simeq 0.4$ μs) and absorbs in the spectral region 350–500 nm ($\lambda_{max} \simeq 405$ nm). The absorption spectrum and a kinetic trace for decay in methanol are shown in Figure 1, parts A and B, respectively. Following the completion of the decay of the short-lived species, a long-lived, broad residual absorption ($\tau \sim 100$ μs) with maximum at 360–370 nm is observed (Figure 1 part C). The 405-nm transient species (Figure 1 part A) is assigned as the triplet of **1**, on the basis of (i) its formation in benzene under energy-transfer sensitization by laser flash photolytically produced PMA triplet or pulse radiolytically produced biphenyl triplet and (ii) its quenching by oxygen, di-*tert*-butylnitroxy (DTBN) radical, azulene, and ferrocene (for quenching rate constants, see Table I). Furthermore, when the laser flash photolysis was carried out in benzene in the presence of 0.1–0.5 mM β-carotene, intense β-carotene triplet absorption was observed at 520–550 nm. Since practically no triplet is produced upon direct light absorption by β-carotene, this observation suggests that a triplet species capable of transfering energy to the polyene is produced upon photoexcitation of **1**. The pseudo-first-order rate constant (k_{obsd}) for the growth[29] of β-carotene absorption is given by: $k_{obsd} = k_0^T + k_q^T$[β-carotene], where k_0^T is the rate constant for the decay of the triplet donor and k_q^T is that for energy transfer to the polyene (acceptor). The slope of the plots of k_{obsd} against [β-carotene], gave a value of 5×10^9 M^{-1} s^{-1} for k_q^T; the intercept, $\sim 2 \times 10^6$ s^{-1}, is close to the reciprocal of the lifetime of the 405 nm species, supporting its assignment as the triplet donor. 1-Methylnaphthalene and 2,5-dimethyl-2,4-hexadiene do not quench it ($k_q < 10^7$ M^{-1} s^{-1} in benzene) suggesting that the triplet energy of **1** is lower than those of the two quenchers (60 and 59 kcal/mol, respectively).[30]

No attempt was made to obtain a definitive assignment of the residual long-lived absorption although, conceivably, it could be attributed to one of the species **2**–**4** (see Scheme I). Interestingly, in methanol and in benzene containing methanol (⩾5%) first-order growths of a photoproduct was observed on a long time scale (~100 μs) in the spectral region 320–440 nm. This is illustrated by the transient absorption spectra in Figure 1 parts D and E (close to the onset and the completion of the growth process in methanol) and the kinetic trace at 390 nm in Figure 1 part F. The rate constant, $(6.4 \pm 0.5) \times 10^4$ s^{-1}, for the growth process in degassed methanol remains practically unchanged when saturated with oxygen; however, the plateau absorbance is decreased. A Stern–Volmer plot was constructed in terms of eq 1, where ΔOD_0 and ΔOD are the

$$\frac{\Delta OD_0}{\Delta OD} = 1 + k_q \tau[Q] \qquad (1)$$

plateau absorbances in the absence and presence of oxygen, τ is the lifetime of the oxygen-quenchable precursor, and k_q is the rate constant for its quenching by oxygen (Table I). The slope of this plot gives a value of 320 M^{-1} for ($k_q\tau$). On the other hand, from τ_T and k_q^T values for the triplet of **1** in methanol (Table I), one would expect a value of 620 M^{-1} for $k_q\tau$, provided the triplet is the precursor of the product responsible for the growth. Thus, the involvement of the triplet is ruled out. This is confirmed by the fact that upon pulse radiolysis of a solution of 0.005 M biphenyl and 2 mM **1** in benzene + 5% methanol, the methanol-related growth process is not observed on a long time scale (200 μs).

The possibility that the slow growth process in methanol is due to hydrogen abstraction from the solvent by the diradicals **2** and **5**, (Scheme I) is untenable because it is not observed in solvents such as cyclohexane or toluene in the laser flash photolysis experiments. Similarly, the transient responsible for the growth cannot be assigned to the radical anion (or ketyl radical) formed by electron transfer from hydroxymethyl radical to the ground state of **1** since (i) the rate of growth is independent of substrate concentrations (0.5–5 mM) and (ii) no transient absorption was observed at 350–400 nm, upon pulse radiolysis of **1** in N_2O-saturated methanol.[31] Two other possible explanations may be recognized, namely, (i) addition of methanol to the ketene (similar to **9** in Scheme II), formed as a result of intramolecular phenyl group transfer, and (ii) methanol assisted proton transfer in **4**, leading to its enolization (Scheme I). The former possibility is unlikely, since no methyl ester, analogous to **12** (Scheme II) was isolated in measurable yields in attempted steady-state photolysis experiments of **1** in methanol.

The quantum yield of triplet formation (Φ_T) for **1** in benzene was measured[32] by energy transfer to β-carotene

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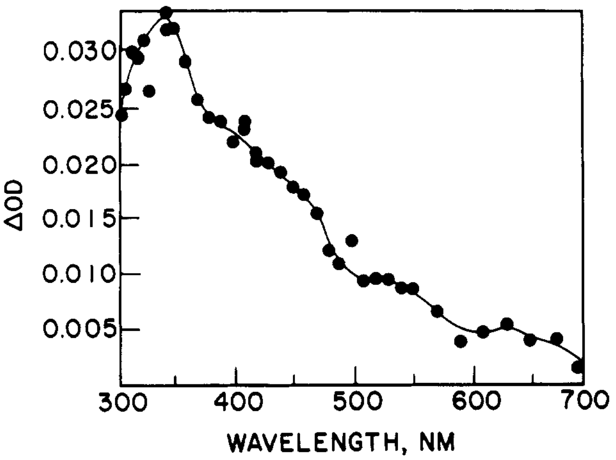

Figure 2. Transient absorption spectrum of 8 in benzene.

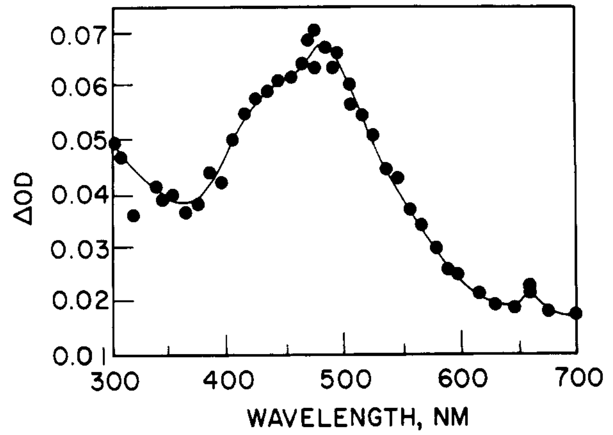

Figure 3. Transient absorption spectrum of 14 in benzene.

using benzophenone triplet formation ($\Phi_T = 1$) in benzene (Table I) as an actinometer. Comparison of the end-of-pulse absorbance changes (ΔOD) due to the triplets of benzophenone (at 532 nm) and 1 (at 410 nm) in solutions optically matched at 337.1 nm and use of the Φ_T data gave an estimate of the extinction coefficient (ϵ_T) of the latter. The following equation was used in the calculation:

$$\epsilon_T{}^S = \left(\frac{\Delta OD_0{}^S}{\Delta OD_0{}^R}\right)\left(\frac{\Phi_T{}^R}{\Phi_T{}^S}\right)\epsilon_T{}^R \qquad (2)$$

The upper subscripts S and R denote the substrate (1) and the reference (benzophenone), respectively. The value of $\epsilon_T{}^R$ was taken to be 7.6×10^3 M^{-1} cm^{-1} at 532 nm in benzene.[33] Assuming that the extinction coefficient of the triplet of 1 in methanol is similar to that in benzene, the Φ_T of 1 in methanol was estimated (Table I).

(b) 7-Oxa-2,3-dibenzoylbicyclo[2.2.1]hept-2-ene (8) and 1,4-Diphenyl-2,3-dibenzoyl-1,4-epoxy-1,4-dihydronaphthalene (14). Laser flash photolysis of 1,4-epoxides 8 and 14 gives transient species with spectral and kinetic features summarized in Table I and illustrated in Figures 2 and 3, respectively. The transients are assigned as triplets based on observations similar to those described in the case of 1. Also, data concerning Φ_T and ϵ_T (Table I) were obtained by the comparative methods as outlined in the case of 1. The quality of signals due to the triplet absorption in the case of 8 in both methanol and benzene was poor, apparently owing to their small extinction coefficients at 400–500 nm.

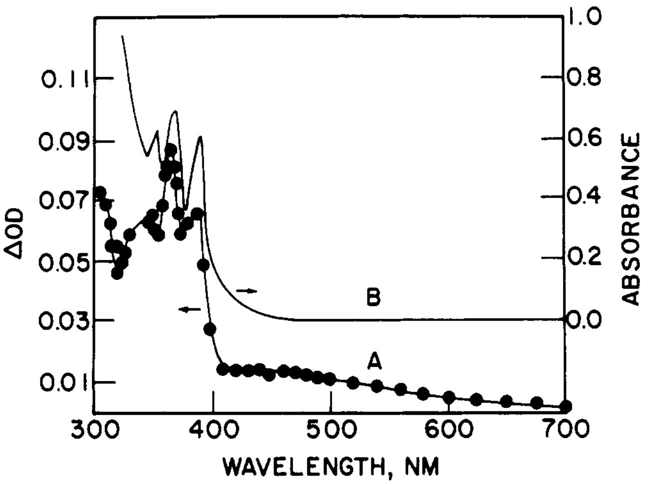

Figure 4. (A) Absorption spectrum of photoproduct of 24 formed 2 μs after the laser pulse in benzene; (B) absorption spectrum of isolated photoproduct 25 in benzene.

An additional longer-lived transient species was observed in the case of 14; this absorbed in the short wavelength region (300–380 nm) and showed only 5–10% decay over ~100 μs. It is possible that this species is related with the diradical intermediate 15, implicated in the formation of the major photoproduct 17 obtained by steady-state photolysis.

(c) 9,10-Dihydro-9,10-(1,2-dibenzoyl-1,2-epoxyethano)anthracene (24). Laser excitation of 1,2-epoxide 24 in both methanol and benzene results in the formation of a "permanent" photoproduct, characterized by a structured absorption spectrum (Figure 4 part A). The "permanent" nature (i.e., lack of decay) as well as its formation via a triplet route was established by generating the species under sensitization by pulse radiolytically produced acetophenone triplet in benzene and observing it over ~100 ms. A similar spectrum was also obtained under sensitization by laser flash photolytically produced PMA triplet which, as mentioned earlier, was effectively quenched by 24. There is a peak-by-peak correspondence of the time-resolved spectrum of the photoproduct seen in pulse radiolysis and laser flash photolysis with the absorption spectrum (Figure 4 part B) of the final product 25 isolated in the steady-state photolysis. This suggests that the latter is formed fast, almost within the laser pulse, via very short-lived intermediates. Furthermore, our results based on energy-transfer sensitization clearly indicate that the triplet of 24 can be involved in its phototransformation to 25.

In order to shed more light on the triplet intermediate of 24, the following experiments were carried out. (i) A solution of 24 was flash photolyzed in the presence of varying concentrations of 1-methylnaphthalene (0.01–0.15 M) and the triplet of the latter with its characteristic spectrum (λ_{max} = 425 nm) was formed as a result of energy transfer from the short-lived triplet of 24. Note that under the conditions of our experiment, the laser photons were absorbed exclusively by 24. (ii) 2,5-Dimethyl-2,4-hexadiene, added up to 70 mM, was found to lower the yield of the "permanent" photoproduct, 25 (monitored at 400 nm). Based on the mechanism that the triplet of 24 acting as a precursor for 25 is being quenched by the diene, a Stern–Volmer plot was constructed in terms of eq 1, where the quencher is the diene. The plot, shown in Figure 5, does not exhibit any significant curvature, suggesting that

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[32] For details, see: Kumar, C. V.; Qin, L.; Das, P. K. *J. Chem. Soc. Faraday Trans 2* **1984**, *80*, 783–793.

[33] Bensasson, R.; Land, E. J. *Photochem. Photobiol. Rev.* **1978**, *3*, 163–191.

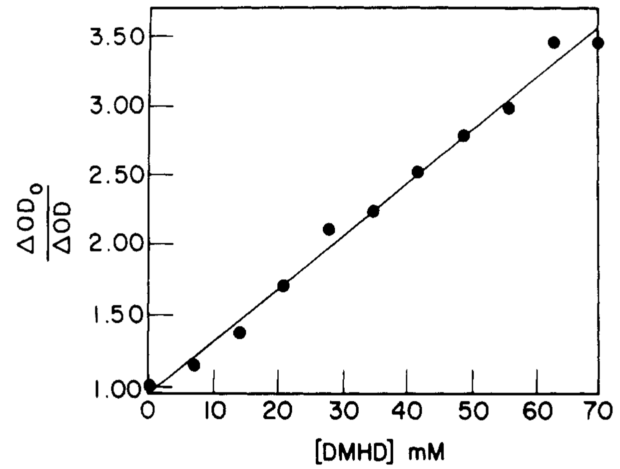

Figure 5. Stern–Volmer plot for the quenching of triplet precursor of photoproduct **25** by DMHD in benzene, based on eq 1.

the quenching of a single precursor, i.e., the triplet of **24**, is involved. The slope ($k_q{}^T\tau_T$) of the plot is 35 M^{-1}; based on a value of 5 × 10^9 M^{-1} s^{-1} for diffusion-controlled, exothermic, energy transfer from the triplet of **24** to the diene, we obtain an extimate of 7 ns for τ_T. (iii) Absorbance changes ΔOD_{MN} due to 1-methylnaphthalene triplet were monitored at 425 nm in the limit of high concentrations (0.05–0.2 M) of the quencher for the triplet of **24**, produced by direct laser excitation in benzene. The intercept of the plot of $[\Delta OD_{MN}]^{-1}$ against $[\text{1-methylnaphthalene}]^{-1}$ was compared with that of a similar plot for the quenching of benzophenone triplet in an optically matched solution in benzene; this gave 1.0 ± 0.1 as the triplet yield of **24** in benzene.

The quantum yields (Φ_P) of laser flash photolytic formation of the photoproduct **25** were determined in benzene and methanol using benzophenone triplet formation in benzene as an actinometer. Surprisingly, Φ_P in benzene (0.34) was about the same as that in methanol (0.28).

The laser flash photolytic transient absorption spectra from **24** in both benzene and methnol also show the formation of a minor transient, absorbing at 450–550 nm (Figure 4 part A). This transient (λ_{max} 460 nm) undergoes ~10% decay over 100 μs under the conditions of our measurements and is not quenched by oxygen, dimethyl acetylenedicarboxylate and maleic anhydride. That this product is triplet mediated is shown by the fact that 2,5-dimethyl-2,4-hexadiene quenches its yield (measured in terms of absorption at 460 nm) with the same Stern–Volmer constant as that found for the permanent photoproduct, **25** (vide supra). An assignment in terms of an ylide formed by the cleavage of the oxirane ring seems unlikely in view of the lack of reactivity toward dipolarophiles, dimethyl acetylenedicarboxylate, and maleic anhydride. On the other hand, fragmentation of the oxirane moiety, producing a keto carbene seems plausible.

Experimental Section

All melting points are uncorrected and were determined on a Mel-Temp melting point apparatus. The IR spectra were recorded on Perkin-Elmer Model 377 or Model 580 infrared spectrophotometers. The electronic spectra were recorded on Cary 17D, Cary 219, or Beckman DB spectrophotometers. The ^{1}H NMR spectra were recorded on Varian A-60, XL-100, JEOL-100, or WH-270 NMR spectrometers. The mass spectra were recorded on a Hitachi RMU-6E single-focusing mass spectrometer or a Varian Mat CH7 mass spectrometer at 70 eV. Steady-state irradiations were carried out in a Srinivasan-Griffin Rayonet photochemical reactor (3500 Å) or by using a Hanovia 450-W medium-pressure mercury lamp in a quartz-jacketted immersion well.

Starting Materials. DBA (**6**),[34,35] mp 110–111 °C, 9,10-dihydro-9,10-(1,2-dibenzoyletheno)anthracene,[36] mp 212 °C, **1**,[36] mp 122–123 °C, **8**,[37] mp 92 °C, and **14**,[36] mp 157 °C, were prepared by reported procedures. Solvents for steady-state photolysis studies were purified and distilled before use, whereas Aldrich Gold Label solvents were used for laser studies. Petroleum ether used was the fraction with bp 60–80 °C.

Preparation of 9,10-Dihydro-9,10-(1,2-dibenzoyl-1,2-epoxyethano)anthracene (24). To a solution of 9,10-dihydro-9,10-(1,2-dibenzoyletheno)anthracene (1.0 g, 2.3 mmol) in ethanol (150 mL) was added an ethanolic solution of potassium hydroxide (0.14 g, 2.5 mmol in 10 mL) containing 30% aqueous hydrogen peroxide (2 mL). The mixture was refluxed for 5 min and left at room temperature for 12 h. After removal of the solvent under vacuum, the residue was washed with water and recrystallized from a mixture (9:1) of benzene and ethyl acetate to give 0.7 g (70%) of **24**, mp 212 °C: IR ν_{max} (KBr) 3024, 3014, 2984 and 2974 (CH), 1663 (C═O), 1593 and 1578 (C═C) cm^{-1}; UV λ_{max} (ethanol) 252 nm (ε 26 300), 330 (850); ^{1}H NMR (CDCl$_3$) δ 5.00 (2 H, s, bridgehead), δ 7.33 (18 H, m, aromatic); mass spectrum, *m/e* (relative intensity) 428 (M^+, 27), 323 ($M^+ - COC_6H_5$, 90), 295 ($M^+ - COC_6H_5 - CO$, 100) and other peaks.

Anal. Calcd for $C_{30}H_{20}O_3$: C, 84.12; H, 4.67. Found: C, 84.03; H, 4.62.

Irradiation of 7-Oxa-2,3-dibenzoylbicyclo[2.2.1]hepta-2,5-diene (1). A solution of **1** (0.5 g, 1.6 mmol) in benzene (250 mL) was irradiated under a 450-W Hanovia medium-pressure mercury lamp for 2.5 h and the photolysis was repeated several times to photolyze, in all, 2.5 g (8 mmol). After removal of the solvent, the residual solid was chromatographed over silica gel. Elution with a mixture (1:20) of benzene and petroleum ether gave 0.25 g (13%) of DBA (**6**), mp 110–111 °C (mixture melting point). Further elution with a mixture (1:1) of benzene and petroleum ether gave 0.8 g (32%) of **3**, mp 172 °C, after recrystallization from a mixture (1:5) of benzene and cyclohexane: IR ν_{max} (KBr) 3120 (OH), 2870 (CH), 1675 (C═O), 1600 and 1575 (C═C) cm^{-1}; UV λ_{max} (ethanol) 244 nm (ε 16 000) 268 (19 000), 298 (19 500) and 360 (6400); ^{1}H NMR (CDCl$_3$) δ 7.45 (12 H, m, aromatic and vinylic), 9.75 (1 H, s, formyl), 18.9 (1 H, s, D$_2$O exchangeable, enolic);[38] mass spectrum, *m/e* (relative intensity) 302 (M^+, 8) 273 ($M^+ - CHO$, 1), 168 ($M^+ - CHO - COC_6H_5$, 1) and other peaks.

Anal. Calcd for $C_{28}H_{14}O_3$: C, 79.47; H, 4.63. Found: C, 79.66; H, 4.45.

Irradiation of 7-Oxa-2,3-dibenzoylbicyclo[2.2.1]hept-2-ene (8). A solution of **8** (0.3 g, 1 mmol) in methanol (300 mL) was irradiated for 2.5 h under a 450-W Hanovia medium-pressure mercury lamp. After removal of the solvent under vacuum, the residue was fractionally crystallized from a mixture (1:2) of benzene and methanol to give 60 mg (22%) of DBA (**6**), mp 111 °C (mixture melting point) and **12**, mp 132–133 °C: IR λ_{max} (KBr) 3060, 2980 and 2940 (CH), 1725 (C═O) cm^{-1}; UV λ_{max} (methanol) 260 nm (ε 18 000); ^{1}H NMR (CDCl$_3$) δ 3.30 (3 H, s, methoxy), 7.05 (10 H, m, aromatic), 5.10 (1 H, q, J = 3.2 Hz, J' = 2.4 Hz, H^4 proton), 3.90 (1 H, q, J = 5.6 Hz, J' = 1.6 Hz, H^2 proton), 4.85 (1 H, t (merged), J = 5.6 Hz, H^1 proton), 1.92 (4 H, m, H^5 and H^6 protons);[39] mass spectrum, *m/e* (relative intensity) 336 (M^+, 100), 304 ($M^+ - CH_3OH$, 29), 277 ($M^+ - CO_2CH_3$, 41) and other peaks.

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(38) The observed downfield shift of the enolic proton in **3** is consistent with the reported values for the enolic protons in hydroxyfulvenes. See: (a) Stusche, D.; Prinzbach, H. *Chem. Ber.* **1973**, *106*, 3817–3823. (b) Bansal, R. K.; McCulloch, A. W.; Rasmussen, P. W.; McInnes, A. G. *Can. J. Chem.* **1975**, *53*, 138–142.

(39) These assignments have been supported by proton decoupling experiments. Thus, irradiation of H^1 resulted in the simplification of the multiplet at δ 1.92 and the quartet at δ 3.90, whereas irradiation of H^4 resulted in the simplification of the multiplet at δ 1.92 only. Further, the small coupling (1.6 Hz) of H^2, falling in the range of W coupling observed in such systems, necessitates the exo positioning of the proton, as in **12**.

Anal. Calcd for $C_{21}H_{20}O_4$: C, 75.01; H, 5.94. Found: C, 74.82; H, 5.50.

Irradiation of 1,4-Diphenyl-2,3-dibenzoyl-1,4-dihydro-1,4-epoxynaphthalene (14). A solution of **14** (0.5 g, 1 mmol) in benzene (250 mL) was irradiated for 0.75 h under a 450-W Hanovia medium-pressure mercury lamp. The experiment was repeated several times to irradiate, in all, 5 g (10 mmol) of **14**. After removal of the solvent from the combined photolysates, the residual solid was chromatographed over silica gel. Elution with petroleum ether gave 50 mg (2%) of **20**, mp 130 °C (mixture melting point).

Further elution with a mixture (1:4) of benzene and petroleum ether gave 1.25 g (25%) of the lactone **17**, mp 236 °C, after recrystallization from a mixture (1:4) of methylene chloride and petroleum ether: IR ν_{max} (KBr) 3050, 3020 and 3000 (CH), 1780 (C=O), 1590 (C=C) cm^{-1}; UV λ_{max} (ethanol) 256 nm (ϵ 46 000), 300 (3000), 347 (3500); ^{1}H NMR ($CDCl_3$) δ 7.16 (m, aromatic protons); mass spectrum, *m/e* (relative intensity) 504 (M^+, 1), 460 ($M^+ - CO$, 1), 411 ($M^+ - C_6H_5 - O$, 100) and other peaks.

Anal. Calcd for $C_{36}H_{24}O_3$: C, 85.70; H, 4.78. Found: C, 86.10; H, 4.66.

Further elution of the column with a mixture (1:1) of benzene and petroleum ether gave 0.3 g (10%) of **23**, mp 149–150 °C (mixture melting point).

Thermolysis of 1,4-Diphenyl-2,3-dibenzoyl-1,4-dihydro-1,4-epoxynaphthalene (14). A sample of **14** (0.5 g, 1 mmol) was heated at ca. 320 °C for 3 h. The reaction mixture was chromatographed over silica gel. Elution with petroleum ether gave 25 mg (10%) of **20**, mp 130 °C (mixture melting point). Further elution with a mixture (1:9) of benzene and petroleum ether gave 10 mg (4%) of **23**, mp 149–150 °C (mixture melting point). Continued elution with a mixture (1:4) of benzene and petroleum ether gave 80 mg (16%) of **22**, mp 202 °C, after recrystallization from a mixture (1:3) of benzene and petroleum ether: IR ν_{max} (KBr) 3060 and 3020 (CH), 1740 (C=O, ester), 1658 (C=O, ketone) cm^{-1}; UV λ_{max} (chloroform) 248 nm (ϵ 1800) and 284 (9700); ^{1}H NMR ($CDCl_3$) δ 7.40 (m, aromatic); mass spectrum, *m/e* (relative intensity) 504 (M^+, 100), 399 ($M^+ - COC_6H_5$, 5), 383 ($M^+ - OCOC_6H_5$, 3) and other peaks.

Anal. Calcd for $C_{36}H_{24}O_3$: C, 85.71; H, 4.76. Found: C, 85.30; H, 4.49.

Hydrolysis of 22. A mixture of **22** (200 mg, 0.4 mmol) and potassium hydroxide (280 mg, 5 mmol) in ethanol (25 mL) was refluxed for 3 h. After removal of the solvent, the residual solid was extracted with methylene chloride. Removal of the solvent gave 50 mg (33%) of **21**, mp 124 °C, after recrystallization from a mixture (1:4) of benzene and petroleum ether: IR ν_{max} (KBr) 3520 (OH), 3060 and 3020 (CH), 1680 (C=O) cm^{-1}; UV λ_{max} (ethanol) 230 nm (ϵ 43 000), 287 (32 000) and 340 (18 000); ^{1}H NMR ($CDCl_3$) δ 5.80 (1 H, s, D_2O exchangeable hydroxy proton), 7.35 (19 H, m, aromatic); mass spectrum, *m/e* (relative intensity) 400 (M^+, 100), 383 ($M^+ - OH$, 3), 372 ($M^+ - CO$, 2), 323 ($M^+ - C_6H_5$, 19), 295 ($M^+ - COC_6H_5$, 21) and other peaks.

Anal. Calcd for $C_{29}H_{20}O_2$: C, 87.00; H, 5.00. Found: C, 86.50; H, 4.67.

Benzoylation of 21. A mixture of **21** (50 mg, 0.13 mmol) in dry benzene (5 mL), benzoyl chloride (140 mg, 1 mmol), and dry pyridine (0.5 mL) was refluxed for 6 h. Subsequently, it was diluted with 50 mL of benzene and was filtered through a column of alumina. After removal of the solvent, the solid residue was chromatographed over silica gel. Elution with benzene gave 40 mg (60%) of **22**, mp 202 °C (mixture melting point).

Irradiation of 9,10-Dihydro-9,10-(1,2-dibenzoyl-1,2-epoxyethano)anthracene (24). A solution of **24** (1.5 g, 3.5 mmol) in benzene was irradiated for 10 min under a 450-W Hanovia medium-pressure mercury lamp. After removal of the solvent, the solid residue was chromatographed over neutral alumina. Elution with benzene gave 115 mg (7%) of **24**, mp 210–211 °C (mixture melting point), after recrystallization from a mixture (1:2) of benzene and petroleum ether. Further elution with benzene gave 1.0 g (66%) of **25**, mp 189–190 °C, after recrystallization from carbon tetrachloride: IR ν_{max} (KBr) 3280 (OH hydrogen bonded) 3060 (CH), 1680 (C=O); UV λ_{max} (cyclohexane) 236 nm (ϵ 1400), 260 (10 000), 316 (14 000), 332 (14 000) 352 (8500), 372 (9000), 392 (8000), 404 (2400); ^{1}H NMR ($CDCl_3$) δ 4.77 (1 H, s, D_2O exchangeable, enolic hydroxy proton), 7.68 (18 H, m, aromatic); mass spectrum, *m/e* (relative intensity) 428 (M^+, 2) 411 ($M^+ - OH$, 1) 323 ($M^+ - COC_6H_5$, 1) and other peaks.

Anal. Calcd for $C_{30}H_{20}O_3$: C, 84.12; H, 4.67. Found: C, 83.70; H, 4.43.

In a repeat run, a solution of **24** in methanol (70 mL was irradiated for 0.5 h under an RPR (3500 Å) light source and worked up as in the earlier case to give 100 mg (50%) of the unchanged starting material (**24**), mp 210–211 °C (mixture melting point), and 40 mg (20%) of **25**, mp 189–190 °C (mixture melting point).

Thermolysis of 24. A sample of **24** (1.5 g, 3.5 mmol) was heated at ca. 230 °C for 20 min. The reaction mixture was chromatographed over neutral alumina. Elution with benzene gave 375 mg (25%) of the unchanged **24**, mp 212 °C (mixture melting point), after recrystallization from a mixture (1:2) of benzene and petroleum ether. Further elution with benzene gave 560 mg (38%) of **25**, mp 189–190 °C (mixture melting point), after recrystallization from carbon tetrachloride.

Acetylation of 25. A mixture of **25** (100 mg, 0.25 mmol), acetic anhydride (2 mL, excess), and pyridine (2 mL) in dry benzene (15 mL) was refluxed for 8 h and poured on to crushed ice. The benzene layer was washed with dilute hydrochloric acid and then with water. Removal of the solvent gave a residue, which was chromatographed over neutral alumina. Elution with benzene gave 70 mg (71%) of **28**, mp 226–227 °C, after recrystallization from carbon tetrachloride: IR ν_{max} (KBr) 3060 (CH), 1760 (C=O, ester), 1720 (C=O, keto); UV λ_{max} (methanol) 256 nm (ϵ 82 000), 332 (43 000), 380 (32 000); ^{1}H NMR ($CDCl_3$) δ 2.30 (3 H, s, methyl protons), 7.65 (19 H, m, aromatic); mass spectrum, *m/e* (relative intensity) 470 (M^+, 100), 428 ($M^+ - CH_2CO$, 2), 323 ($M^+ - CH_2CO - COC_6H_5$, 96), 295 ($M^+ - CH_2CO - COC_6H_5 - CO$, 80), 218 ($M^+ - CH_2CO - COC_6H_5 - COC_6H_5$, 10) and other peaks.

Anal. Calcd for $C_{32}H_{22}O_4$: C, 81.70; H, 4.68. Found: C, 81.32; H, 4.68.

Laser Flash Photolysis. Pulse excitation was carried out at 337.1 nm (2–3 mJ, ~8 ns, UV 400 Molectron Nitrogen laser). The transient phenomena were observed in 3 × 7 mm quartz cells using a kinetic spectrometer, described elsewhere.[40] The solvents employed were benzene and methanol and unless oxygen effects were meant to be studied, the solutions were deoxygenated by purging thoroughly with argon or nitrogen. In the experiments where a large number of laser shots were necessary, e.g., for wavelength-by-wavelength measurements of transient absorption spectra, a flow system was used in which the solution for photolysis was allowed to drain from a reservoir through the cell. This was particularly necessary for epoxide **24**; in this case, the major photoproduct, anthracene derivative **25**, accumulating in the solution in the course of photolysis, led to an intense and sharp transient absorption due to its triplet (λ_{max} 430 nm).

For kinetic studies of oxygen quenching, 3–4 oxygen concentrations in the range 0.4–4 mM were used.

Pulse Radiolysis. The computer controlled pulse radiolysis apparatus, which allows determination of transient spectra at various times after the pulse and kinetic measurements of the spectral changes have been described earlier.[41]

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