SO_3 in nitromethane (7.0 mL). After 30 min 1.0 mL of D_2O was added and the mixture heated for 20 min at 60 °C to hydrolyze most of the sulfate and any anhydride. The aqueous layer was isolated and extracted at room temperature three times with CH_2Cl_2 (1-2 mL) to remove any unreacted substrate and remaining solvent. Residual CH_2Cl_2 was removed by bubbling N_2 through the aqueous solution for 30 min. Then for the product analysis an ^1H NMR spectrum was recorded. In some cases the D_2O solution of the sulfonic acids was neutralized with dilute aqueous potassium hydroxide, the solvents were removed by freeze drying, and an ^1H NMR spectrum was recorded of the remaining mixture of potassium sulfonates in D_2O.

E. The sulfonation of **1**, **2**, and **5** (0.50 M) in sulfuric acid of the desired strength was followed by recording ^1H NMR spectra of the homogeneous sulfuric acid solutions after appropriate time intervals. The solubility of **2** and its sulfonic acids was too low to study the sulfonation of **2** at acid concentrations lower than 98% H_2SO_4. The composition of the reaction mixtures was determined by multicomponent ^1H NMR analysis.[13] The conversion of **1** and **5** was first order in the substrate, the plots of log [ArH] vs. time being linear up to at least 50% conversion.

Acknowledgment. The authors thank H. D. Goossens for assistance and Dr. K. Laali for a gift of 2,6-diisopropylphenol.

Registry No. **1**, 576-26-1; **1**-OSO_3H, 92545-08-9; **2**, 2078-54-8; **2**-OSO_3H, 92545-09-0; **3**, 128-39-2; **4**, 87-65-0; **4**-OSO_3H, 92545-10-3; **5**, 1004-66-6; **6**, 108-95-2; **6**-OSO_3H, 937-34-8; **7**, 100-66-3.

Supplementary Material Available: Table I listing the ^1H NMR parameters of **1**-**6** and their sulfo derivatives (3 pages). Ordering information is given on any current masthead page.

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

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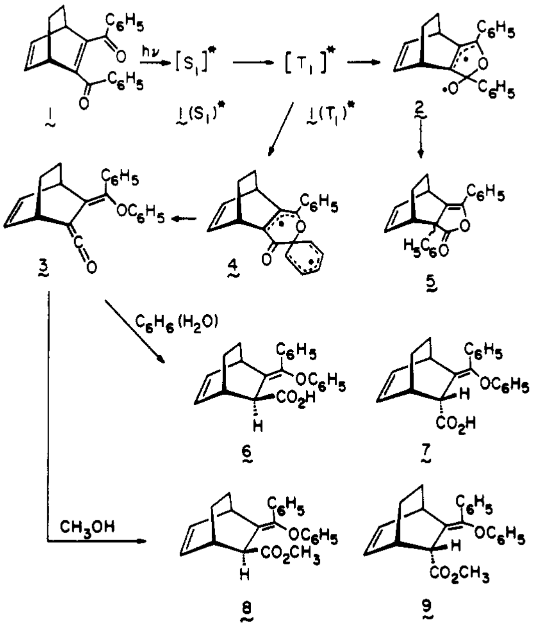
Phototransformations of the dibenzobarrelenes **10**, **11**, and **23**, prepared by the reaction of the appropriate anthracenes with dibenzoylacetylenes, are reported. Irradiation of **10** and **11** in solvents such as benzene, methanol, and acetone gave the corresponding dibenzosemibullvalenes, **17** and **18**, respectively, in good yields. These dibenzosemibullvalenes on catalytic hydrogenation using 5% Pd on charcoal gave the corresponding cyclopropane ring-opened products, **21** and **22**, respectively. Irradiation of **23** in benzene gave a mixture of 2,3-dibenzoyl-2,3-dihydro-1,4-dimethyl-2,3-benzonaphthalene (**27**, 12%), 1,4-dibenzoyl-5,8-dimethyl-2,3:6,7-dibenzocyclooctatetraene (**24**, 20%), the carbinol **29** (45%), and benzoic acid (7%). Irradiation of **23** in methanol gave a mixture of **27** (25%), **24** (27%), and benzoic acid (8%). Laser flash photolysis (337.1 nm) of **10**, **11**, and **23** led to transient species, characterized by strong absorptions in the 300-650-nm region. These transients are due to the triplet states of the substrates, as established by quenching studies involving oxygen, di-*tert*-butylnitroxide, azulene, and β-carotene. Energy-transfer sensitization of **10**, **11**, and **23** by benzophenone in benzene also gave rise to the same transients, as formed under direct irradiation. The quantum yields of triplet formation (Φ_T) were estimated to be high for **10** and **11** (~1), whereas it is significantly lower for **23** (~0.7).

Introduction

It has been reported earlier that dibenzoylethylenes undergo an interesting photorearrangement in protic solvents such as alcohols, besides cis-trans isomerization, which results in the corresponding butenoic esters.[3-7] Recent studies have shown that *cis*-1,2-dibenzoylalkenes, having rigid structural features and wherein the cis-trans isomerization is prevented, undergo the photorearrangement predominantly.[8] Thus, the photolysis of 2,3-dibenzoylbicyclo[2.2.2]octa-2,5-diene (**1**), for example, gave a mixture of 6-(1-phenoxy-1-phenylmethylene)bicyclo[2.2.2]oct-2-ene-5-*exo*-carboxylic acid (**6**), 6-(1-phenoxy-1-phenylmethylene)bicyclo[2.2.2]oct-2-ene-5-*endo*-carboxylic acid (**7**), and the lactone **5**, whereas irradiation of **1** in methanol gave a mixture of methyl 6-(1-phenoxy-1-phenylmethylene)bicyclo[2.2.2]oct-2-ene-5-*exo*-

Scheme I



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[1] Document No. NDRL-2579 from the Notre Dame Radiation Laboratory.

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0022-3263/84/1949-4923$01.50/0

carboxylate (**8**) and methyl 6-(1-phenoxy-1-phenylmethylene)bicyclo[2.2.2]oct-2-ene-5-*endo*-carboxylate (**9**). Laser flash photolysis studies[8] have shown that the phototransformations of **1**, giving rise to the different products, may involve diradical intermediates such as **2** and **4**, shown in Scheme I.

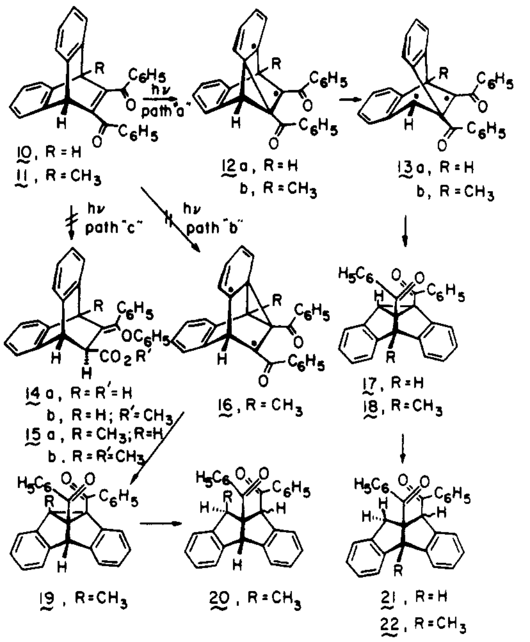
The object of the present investigation has been to examine the photochemical transformations of some selected examples of *cis*-1,2-dibenzoylalkenes, having structural features, which could significantly alter the course of the dibenzoylalkene type of rearrangement. In this connection, we have examined the phototransformations of a few dibenzobarrelenes containing 1,2-dibenzoylalkene moieties such as 11,12-dibenzoyl-9,10-dihydro-9,10-ethenoanthracene (**10**), 11,12-dibenzoyl-9,10-dihydro-9-methyl-9,10-ethenoanthracene (**11**), and 11,12-dibenzoyl-9,10-dihydro-9,10-dimethyl-9,10-ethenoanthracene (**23**). Examination of the structural features of the dibenzobarrelenes, **10**, **11**, and **23**, reveals that they can exhibit photochemical properties, characteristic of both dibenzobarrelenes and *cis*-1,2-dibenzoylalkenes. It may be pointed out here that dibenzobarrelenes are known to undergo di-π-methane rearrangement[9] to give the corresponding semibullvalene derivatives.[10] It therefore was of interest to us to examine the phototransformations of **10**, **11**, and **23**, to study the mode of rearrangement in these substrates. Of particular interest was to examine the nature of the intermediates involved in these transformations through laser flash photolysis technique.

Results and Discussion

1. Preparative Photochemistry and Product Identification. Irradiation of a benzene solution of **10** for 4 h gave a 88% yield of 8c,8d-dibenzoyl-4b,8b,8c,8d-tetrahydrodibenzo[*a,f*]cyclopropa[*c,d*]pentalene (**17**), whereas the irradiation of **10** in methanol for $^1/_2$ h gave a 52% yield of **17**, along with a small amount (8%) of benzoic acid and a 32% recovery of the unchanged starting material (**10**). When the irradiation of **10**, however, was carried out in oxygen-saturated methanol, for $^1/_2$ h, a 47% yield of **17** and a 22% yield of benzoic acid were obtained, besides the recovery of 21% of the unchanged starting material. On the other hand, when the irradiation of **10** was carried out in acetone for $^1/_2$ h, a 89% yield of **17** was isolated.

The irradiation of an unsymmetrically substituted barrelene such as 11,12-dibenzoyl-9,10-dihydro-9-methyl-9,10-ethenoanthracene (**11**) in benzene for $^1/_2$ h gave a 54% yield of 8c,8d-dibenzoyl-4b,8b,8c,8d-tetrahydro-4b-methyldibenzo[*a,f*]cyclopropa[*c,d*]pentalene (**18**) and a small amount (12%) of benzoic acid. Better mass balances, however, were observed when the photolyzed mixtures were gas chromatographically analyzed (see, Experimental Section). Similarly, the irradiation of **11** in methanol gave a 50% yield of **18** and a 8% yield of benzoic acid, whereas the irradiation in acetone, under analogous conditions, gave a 64% yield of **18** and a 8% yield of benzoic acid.

Scheme II



The structures of the semibullvalenes **17** and **18**, formed from **10** and **11**, respectively, were derived on the basis of analytical results, spectral data, and chemical evidence. Catalytic hydrogenation of **17** with 5% Pd on charcoal in THF gave a 60% yield of 9a,10-dibenzoyl-4b,9,9a,10-tetrahydro-*cis*-indeno[1,2-*a*]indene (**21**). The ^{1}H NMR spectrum of **21** showed two doublets at δ 3.55 (1 H, $J_{9,9'}$ = 17 Hz) and 3.79 (1 H, $J_{9,9'}$ = 17 Hz), which have been assigned to the two methylene protons at C-9 position. In addition, the spectrum showed two singlets at δ 5.69 (1 H) and 5.87 (1 H), which have been assigned to the H^{4b} and H^{11} protons, respectively. The aromatic protons appeared as two complex multiplets centered at δ 7.29 (14 H) and 7.87 (4 H), respectively. The ^{13}C NMR spectrum and the mass spectral fragmentations of **21** were in agreement with the assigned structure.

Similarly, catalytic hydrogenation of **18** over 5% Pd on charcoal in THF gave a product, identified as *cis*-9a,10-dibenzoyl-4b,9,9a,10-tetrahydro-4b-methyl-*cis*-indeno[1,2-*a*]indene (**22**). The structure of **22** has been arrived at, on the basis of analytical results and spectral data. The ^{1}H NMR spectrum of **22**, for example, showed a singlet at δ 1.69 (3 H) due to the methyl group at the C-4b position and a second singlet at δ 6.37 (1 H) due to the methine proton at H^{10}. In addition, the spectrum showed two doublets at δ 3.09 (1 H, $J_{9,9'}$ = 18 Hz) and 3.32 (1 H, $J_{9,9'}$ = 18 Hz), respectively, due to the geminal hydrogens at H^9 and $H^{9'}$. The aromatic protons appeared as a complex multiplet centered at δ 7.25 (18 H). It might be pointed out here that if the structure of the photoproduct derived from **11** were to be represented by **19**, wherein the methyl group is at the C-8b position, then **20** would have resulted as the hydrogenation product and the ^{1}H NMR results are not in agreement with this possibility (Scheme II).

A probable mechanism for the formation of the dibenzosemibullvalenes **17** and **18** in the photoreactions of **10** and **11**, respectively, which is in tune with the earlier reported mechanism for the barrelene rearrangement[11] is shown in Scheme II. It is assumed that the excited triplet state of the starting dibenzobarrelene **10** (or **11**) leads

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(9) For some recent reviews, see: (a) Hixon, S. S.; Mariano, P. S.; Zimmerman, H. E. *Chem. Rev.* **1973**, *73*, 531–551. (b) Zimmerman, H. E. In "Rearrangements in Ground and Excited States"; de Mayo, P., Ed.; Academic Press: New York, 1980; Vol. 3, pp 131–166.

(10) For some examples of the di-π-methane rearrangements of dibenzobarrelenes, see: (a) Ciganek, E. *J. Am. Chem. Soc.* **1966**, *88*, 2882–2883. (b) Hart, H.; Murray, R. K., Jr. *J. Am. Chem. Soc.* **1969**, *91*, 2183–2184. (c) Hart, H.; Love, G. M. *J. Am. Chem. Soc.* **1973**, *95*, 4592–4599. (d) Richards, K. E.; Tilman, R. W.; Wright, G. J. *Aust. J. Chem.* **1975**, *28*, 1289–1300. (e) Paddick, R. G.; Richards, K. E.; Wright, G. J. *Aust. J. Chem.* **1976**, *29*, 1005–1015. (f) Cristol, S. J.; Kaufman, R. L.; Opitz, S. M.; Szalecki, W.; Bindel, T. H. *J. Am. Chem. Soc.* **1983**, *105*, 3226–3242. (g) Adam, W.; DeLucchi, O.; Peters, K.; Peters, E.-M.; von Schnering, H. G. *J. Am. Chem. Soc.* **1982**, *104*, 5747–5753.

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initially to the diradical intermediate **12a** (or **12b**), through a benzo–vinyl bridging. Subsequent transformation of **12a** (or **12b**) leads to the dibenzosemibullvalene **17** (or **18**), presumably through a second diradical intermediate **13a** (or **13b**) (path "a", Scheme II). In the case of the unsymmetrically substituted dibenzobarrelene, **11**, however, there could be an alternative pathway for the photoreaction (path "b", Scheme II) involving diradical intermediate **16**, leading ultimately to the C-8b-methyl derivative **19**. The predominant formation of **18** in the photoisomerization of **11** would suggest that of the two possible pathways involving diradicals, **12b** (path "a") and **16** (path "b"), arising through an initial benzo–vinyl bridging, path "a" involving **12b** seems to be preferred. It may be mentioned in this connection that the regioselectivity observed in the photorearrangement of 1-methylbenzonorbornadiene[12] appears to be different from that of the 9-methyldibenzobarrelene derivative, **11**.

It is quite surprising to note that both in the cases of **10** and **11**, none of the photorearranged carboxylic acids (**14a** or **15a**) or esters (**14b** or **15b**) could be isolated when the irradiations were carried out in benzene and methanol, respectively. It is therefore evident that the *cis*-1,2-dibenzoylalkene type of rearrangement does not take place in the case of the dibenzobarrelenes **10** and **11** and the reactions in both these cases proceed through the barrelene rearrangement pathway.

In contrast to the photoisomerizations of the dibenzobarrelenes **10** and **11**, the phototransformations of 11,12-dibenzoyl-9,10-dihydro-9,10-dimethyl-9,10-ethenoanthracene (**23**) give rise to a variety of products, depending on the reaction conditions. Irradiation of **23** in methanol for $^1/_4$ h, for example, gave a mixture of products consisting of 2,3-dibenzoyl-2,3-dihydro-1,4-dimethyl-2,3-benzonaphthalene (**27**, 25%), 1,4-dibenzoyl-5,8-dimethyl-2,3:6,7-dibenzocyclooctatetraene (**24**, 27%), and benzoic acid (8%). In addition, 17% of the unchanged starting material (**23**) could also be recovered from this reaction. Irradiation of a benzene solution of **23** for $^1/_2$ h, on the other hand, gave a mixture of products consisting of the carbinol derivative **29** (45%), the cyclooctatetraene derivative **24** (20%), the naphthalene derivative **27** (12%), and benzoic acid (7%).

The structures of the different products such as **27**, **24**, and **29**, formed in the phototransformations of **23**, have been established on the basis of analytical results, spectral data, and chemical evidences. The ^{1}H NMR spectrum of **27**, for example, showed a singlet at δ 1.77 (6 H), assigned to the methyl protons, whereas the olefinic protons appeared as a complex multiplet, centered at δ 6.82 (4 H). The aromatic protons appeared as a multiplet centered around δ 7.36 (14 H). The ^{13}C NMR spectrum of **27** showed several signals at δ 22.88, 60.59, 120.39, 123.58, 126.42, 127.79, 127.91, 131.89, 136.67, 137.45, 153.59, 154.58 and 199.78. Of these, the signal at δ 22.88 has been assigned to the methyl carbons, whereas the signal at δ 60.69 could be assigned to the C-2 and C-3 carbons, which are considerably deshielded due to the attachment of benzoyl groups. The signal due to the carbonyl carbons appeared at δ 199.78, whereas the signals between δ 120.39–154.58 could be assigned to other sp^2 carbons present in **27**. The mass spectral fragmentations of **27** were also in agreement with the assigned structure.

The ^{1}H NMR spectrum of 1,4-dibenzoyl-5,8-dimethyl-2,3:6,7-dibenzocyclooctatetraene (**24**) showed a singlet at δ 2.09 (6 H), due to the methyl protons, whereas the aromatic protons appeared as two sets of complex multiplets, centered at δ 7.30 (14 H) and 8.27 (4 H). The ^{13}C NMR spectrum of **24** showed several signals at δ 23.15, 126.86, 127.11, 127.47, 127.60, 128.68, 129.63, 133.42, 135.17, 136.40, 138.39, 138.97, 141.77, and 197.81. Of these, the signal at δ 23.15 has been assigned to the methyl carbons, whereas the one at δ 197.81 has been assigned to the carbonyl carbons. The remaining signals between δ 126.86 and 141.77 could be assigned to other sp^2 carbons in **24**. The mass spectral fragmentations of **24** were in agreement with the assigned structure.

To examine whether **24** and **27** are interconvertable, we have studied the photolysis of **24**. It has been found that irradiation of a methanol solution of **24** for 10 min gives a 20% yield of **27**. It may also be mentioned in this connection that the photoisomerizations of cyclooctatetraene derivatives are known to give rise to products analogous to **27**.[13]

The IR spectrum of the carbinol **29** showed the presence of an OH band at 3530 cm^{-1} and did not show any carbonyl absorptions. The ^{1}H NMR spectrum of **29** showed a sharp singlet at δ 1.21 (3 H) due to the methyl protons and a second singlet at δ 3.47 (1 H, D$_2$O exchangeable) due to the hydroxyl proton. In addition, the spectrum showed two doublets at δ 4.64 (1 H, $J_{1',1''}$ = 13 Hz) and 5.07 (1 H, $J_{1',1''}$ = 13 Hz) due to the geminal protons of the *exo*-methylene group. The aromatic protons appeared as a complex multiplet centered at δ 7.51 (18 H). The mass spectral fragmentations of **30** were in support of the assigned structure.

The formation of the different products such as **24**, **27**, and **29** in the photoreaction of **23** could be rationalized in terms of the pathway shown in Scheme III. It would be reasonable to assume that the singlet excited state of **23** could bring about a [π^2s + π^2s] type of addition leading to the intermediate **25**, which in turn can undergo thermal reversions, leading to **24** and **27**. The cyclooctatetraene derivative **24** itself could give rise to **27**, under photochemical conditions as has been independently shown in these studies.

A second possible mode of reaction of **23** is the di-π-methane type of reaction, leading to the diradical intermediate **26**, which can subsequently lead to the dibenzosemibullvalene **29**. It would be reasonable to assume that the semibullvalene **28**, containing methyl and benzoyl groups attached to the cyclopropane ring, will undergo a Norrish type II reaction, leading to the enol **30**, presumably arising through the diradical intermediate **31**. The enol **30**, in turn, can give rise to the carbinol **29** (Scheme III).

The formation of small amounts of benzoic acid in the photoreactions of the dibenzobarrelenes **10**, **11**, and **23** may perhaps be through dioxetane intermediates, formed through the reaction of the starting dibenzobarrelenes with singlet oxygen. Singlet oxygen, in turn, could be formed through the quenching of the dibenzobarrelene triplets with small amounts of oxygen, present as a contaminant in these reactions. To confirm this possibility, we have measured the efficiency (ϕ_Δ) of the generation of singlet oxygen through oxygen quenching of the dibenzobarrelene triplets (**10**, **11**, and **23**), employing laser flash photolysis (337.1 nm) and using 1,3-diphenylisobenzofuran as the monitor for singlet oxygen.[14] It has been found that ϕ_Δ values for **10**, **11**, and **23** were 0.72, 0.71, and 0.49, respectively, indicating thereby that singlet oxygen will be generated easily, under the reaction conditions, if oxygen

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(14) Chattopadhyay, S. K.; Kumar, C. V.; Das, P. K. *J. Photochem.* **1984**, *24*, 1–9.

Scheme III

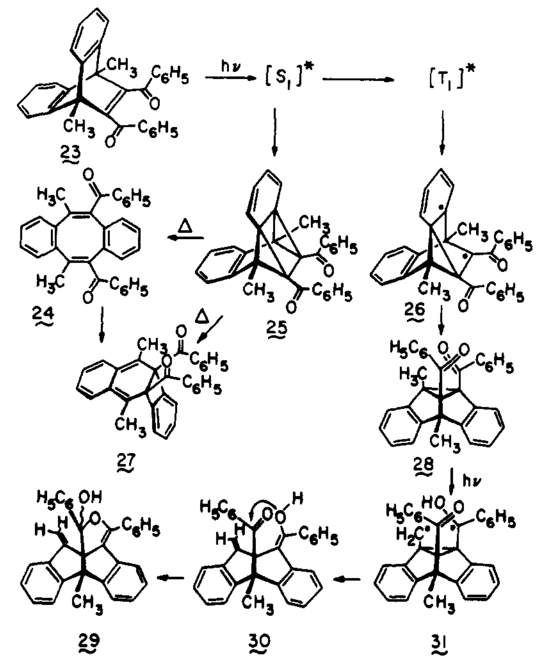

Table I. Spectral and Lifetime Data of the Transients Observed upon Laser Flash Photolysis (337.1 nm) of 10, 11, and 23 in Degassed Benzene and Methanol

no.	solvent	transient λ_{max},[a] nm	τ_T,[b] μs
10	benzene	320, 420, 480	13
	methanol	310, 470, 660	33
11	benzene	320, 420, 460	5.0
	methanol	320, 470, 660	7.3
23	benzene	315, 410, 500	0.8
	methanol	320, 420, ~500	1.6

[a] ±5 nm. [b] ±20%.

Table II. Data Concerning the Triplets of 10, 11, and 23 in Degassed Benzene

				$10^9k_q{}^T$, M^{-1} s^{-1} by[d]			
no.	$10^9k_q{}^T$,[a] M^{-1} s^{-1}	Φ_T[b]	$10^3\epsilon_T$,[c] M^{-1} *cm*$^{-1}$	O$_2$	*azulene*	*β-carotene*	DTBN
10	1.1	0.9	5.5 (480)	0.5	1.5	4.2	0.4
11	0.5	0.9	3.9 (480)	0.45	1.2	3.6	0.2
23	0.28	0.7	5.8 (500)	0.45	0.7	2.9	0.07

[a] Rate constant for the quenching of benzophenone triplet by the substrate; ±15%. [b] ±25%; measured by energy transfer to β-carotene. [c] ±25%. [d] Rate constant for the quenching of the substrate triplets; ±15%.

is present even in small amounts.

2. Laser Flash Photolysis Studies. Laser photolysis experiments were carried out with the pulses (337.1 nm, ~8 ns, up to 3 mJ/pulse) from a nitrogen laser for excitation and a detection system with nanosecond response. The transient spectra produced following pulsed excitation of substrates, **10**, **11**, and **23**, were recorded in benzene and methanol. All showed strong absorptions in the 300–650-nm region. Figure 1 shows a few representative spectra obtained after laser excitation, while Table I summarizes the spectral and lifetime data. Typically the lifetimes were longer in methanol than in benzene.

The transients decay with first-order kinetics at low laser doses (attenuated with neutral density filters) but show considerable second-order contributions at high laser intensities or when the beam is highly concentrated. We propose that the transient signals observed are due to the triplet states of these substrates, and the experiments described below support this assignment.

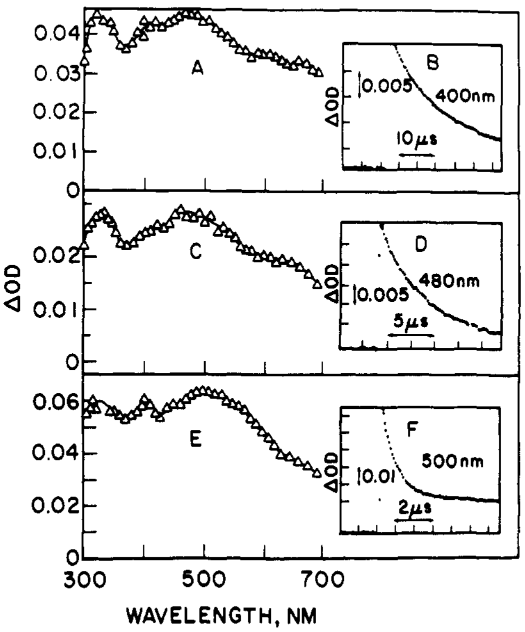

Figure 1. Transient absorption spectra and kinetic traces: (A) T–T absorption spectrum of **10** in benzene; (B) a kinetic trace of **10** at 400 nm in benzene; (C) T–T absorption spectrum of **11** in benzene; (D) a kinetic trace of **11** at 480 nm in benzene; (E) T–T absorption spectrum of **23** in benzene; (F) a kinetic trace of **23** at 500 nm in benzene.

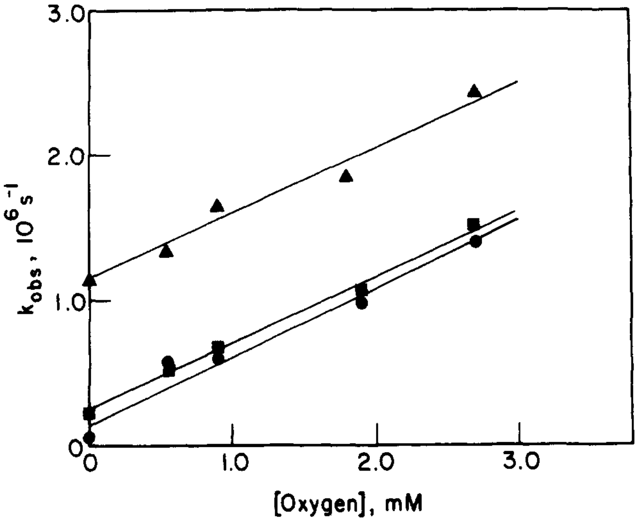

Figure 2. Plots for the oxygen quenching of the triplets of **10** (●), **11** (■), and **23** (▲) in benzene.

Oxygen Quenching. The lifetimes of the transients derived from **10**, **11**, and **23** were examined in benzene at 300 K in the presence of various oxygen concentrations achieved by bubbling custom made mixtures of oxygen and nitrogen. Usually the absorptions were monitored at 480–500 nm for substrate concentrations around 0.5 mM. The values of the bimolecular quenching rate constants have been included in Table II and show moderately efficient quenching and Figure 2 shows the quenching plots.

Quenching by Nitroxides. Persistent free radicals such as dialkyl nitroxides are known to be efficient quenchers of excited states. The substrates studied here are no exception; the quenching plots have been included in Figure 3. The values, which have been included in Table II show efficient but no diffusion-controlled quenching; this is frequently the case for low energy triplet states.

Quenching by Substrates with Low Lying Triplets. Azulene and β-carotene have triplet energies of 39 and

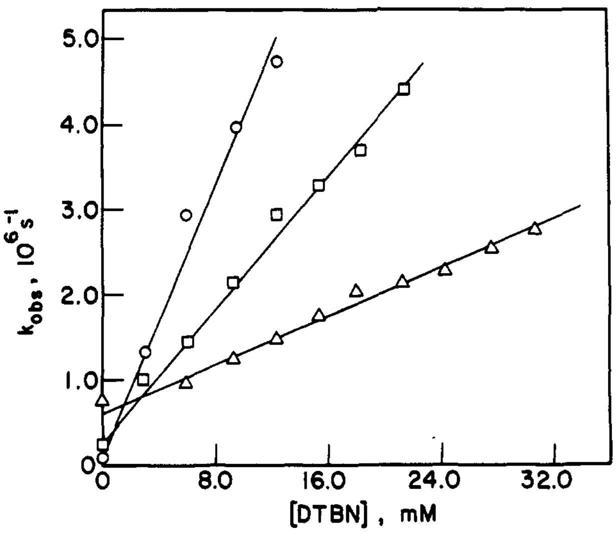

Figure 3. Plots for the DTBN quenching of the triplets of **10** (○), **11** (□) and **23** (△) in benzene.

21–23 kcal/mol, respectively. We find that both these species quench the transients from **10**, **11**, and **23** with rate constants in the neighborhood of 10^9 M^{-1} s^{-1} (see Table II). Transient spectra, monitored following the decay of substrate triplet, reveal the presence of the triplet state of the quencher β-carotene formed in good yields. This is essentially conclusive evidence for the characterization of the transient signals observed from the different dibenzobarrelenes as due to their triplet states. When the plateau absorbances due to β-carotene triplet formation, employing a solution of benzophenone in benzene with matched optical density at 337.1 nm as the reference, were compared, the quantum yields of intersystem crossing (ϕ_T) were estimated[15] as per eq 1. In eq 1, the superscripts R and S

$$\Phi_T^S = \Phi_T^R\left(\frac{\Delta OD^S}{\Delta OD^R}\right)\left(\frac{k_{obsd}^S}{k_{obsd}^S - k_0^S}\right)\left(\frac{k_{obsd}^R - k_0^R}{k_{obsd}^R}\right) \qquad (1)$$

designate reference (benzophenone) and sample, respectively, k_{obsd} is the pseudo-first-order rate constant for the growth of β-carotene triplet, and k_0 is the rate constant for the decay of the donor triplets in the absence of β-carotene, observed in solutions containing benzophenone or sample at the same concentrations as those used for sensitization. Although in these experiments β-carotene absorbed a constant fraction (40–60%) of the laser photons, its direct excitation did not result in any significant triplet formation because of the negligible yield. These values for the triplet quantum yields of **10**, **11**, and **23** have been included in Table II; only in the case of **23**, the value is significantly lower than unity.

The extinction coefficient (ϵ_T^S) of T–T absorption maxima were measured by comparison of end-of-pulse absorbances (ΔOD_0) observed at the respective maxima in the course of the direct laser flash photolysis (337.1 nm) of benzene solutions of benzophenone (reference) and substrates (optically matched at 337.1 nm). The ϵ_T^S values were calculated using the following equation:

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

The superscripts S and R denote the substrate and reference, respectively. The value of ϵ_T^R was taken to be 7.6 × 10^3 M^{-1} cm^{-1} at 532 nm in benzene.[16] The ϵ_T^S values for **10**, **11**, and **23** are included in Table II.

Quenching of Triplet Benzophenone. The triplet state of benzophenone, which lies about 69 kcal/mol above its ground state was readily quenched by the various substrates. The quenching was accomplished by formation of the same transient observed by direct irradiation, a fact that provides further confirmation for the assignment of those species as the corresponding triplet states.

Summary and Conclusions. The triplet triplet absorption spectra of the dibenzobarrelenes **10**, **11**, and **23** show strong absorptions in the 300–650-nm region and strongly suggest that the excitation in these systems is delocalized over the entire barrlene skeleton. The high Φ_T values in the case of **10** and **11** support the experimental observation that only the triplet state derived products, namely the dibenzosemibullvalene derivatives, are formed in these cases. In the case of **23**, however, the Φ_T value is considerably lower and both singlet state and triplet state derived products are observed. The fact that the triplets of the dibenzobarrelenes **10**, **11**, and **23** are efficiently quenched by azulene (E_T = 39 kcal mol^{-1})[17] and other low energy triplet quenchers would suggest that E_T values of these compounds are rather low and perhaps close to 40 kcal mol^{-1}.

Experimental Section

All melting points are uncorrected and were determined on a Mel-Temp melting point apparatus. The IR spectra were recorded on either Perkin-Elmer Model 377 or Model 580 infrared spectrometers. The electronic spectra were recorded on either Beckman DB, Cary 17D, or Cary 219 spectrophotometers. NMR traces were recorded on Varian XL-100 or Bruker WH 270 NMR spectrometers with tetramethylsilane as internal standard. The mass spectra were recorded on a Varian Mat CH 7 mass spectrometer at 70 eV. All irradiation experiments were carried out in a Srinivasan-Griffin Rayonet photochemical reactor (3500 Å) or with a Hanovia 450-W medium-pressure mercury lamp in a quartz-jacketed immersion well. The VPC analyses were carried out by using a glass capillary column (OV-101, 11M H1319A) and hydrogen as carrier gas, on a Packard gas chromatograph, Model 427 III, employing a flame-ionization detector. The analyses were carried out with temperature programming from 100–260 °C (6 °C per min). The irradiations for these studies were carried out in a merry-go-round with a Hanovia 450-W medium-pressure mercury lamp in a quartz-jacketed immersion well, with proper filter solutions (~345-nm lamp source), and in Pyrex reaction tubes.

Starting Materials. Dibenzoylacetylene (DBA),[18,19] mp 110–111 °C, 9-methylanthracene,[20] mp 81 °C, and 9,10-dimethylanthracene,[21] mp 182 °C, were prepared by known procedures. Solvents for photolysis were purified and distilled before use. Petroleum ether used was the fraction with bp 60–80 °C. Aldrich Gold-label solvents were used for laser studies.

Preparation of 11,12-Dibenzoyl-9,10-dihydro-9,10-ethenoanthracenes 10, 11, and 23. The general procedure for the preparation of the ethenoanthracenes involves the addition of an equimolar amount of DBA, in small portions, to a well stirred and equimolar mixture of anthracene and anhydrous aluminum chloride in methylene chloride at room temperature over a period of 10 min. The mixture was stirred for 30 min and poured on to crushed ice and dilute hydrochloric acid. The organic layer was separated, washed with water, and dried. Removal of the

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solvent under vacuum gave the ethenoanthracenes, which were purified by recrystallization from chloroform.

10 (88%): mp 212–213 °C (lit.[22] mp 212–212.5 °C); ^{1}H NMR ($CDCl_3$) δ 5.66 (2 H, s, bridgehead proton), 7.25 (14 H, m, aromatic); ^{13}C NMR ($CDCl_3$) δ 53.81 (bridgehead carbons), 123.77, 125.37, 128.00, 128.39, 132.59, 137.37, 143.90, 153.19, 194.10 (carbonyl carbon).

11 (85%): mp 181 °C (lit.[23] mp 179 °C); ^{1}H NMR ($CDCl_3$) δ 2.09 (3H, s, methyl), 5.64 (1 H, s, bridgehead proton), 7.22 (18 H, m, aromatic); ^{13}C NMR ($CDCl_3$) δ 13.29 (methyl), 52.36 (bridgehead carbon), 52.59 (bridgehead carbon), 121.23, 123.46, 125.03, 125.19, 127.88, 128.19, 128.35, 128.89, 132.44, 133.12, 137.19, 145.45, 146.04, 150.59, 158.23, 193.37 (carbonyl carbon), 195.18 (carbonyl carbon).

23 (83%): mp 262 °C (lit.[23] mp 261–263 °C); ^{1}H NMR ($CDCl_3$) δ 2.11 (6 H, s, methyl), 7.25 (18 H, m, aromatic); ^{13}C NMR ($CDCl_3$) δ 13.48 (methyl), 50.68 (bridgehead carbon), 120.61, 124.73, 128.11, 129.33, 133.36, 136.95, 147.56, 153.65, 195.36 (carbonyl carbon).

Irradiation of 11,12-Dibenzoyl-9,10-dihydro-9,10-ethenoanthracene (10). A solution of 10 (400 mg, 1 mmol) in benzene (200 mL) was irradiated for 4 h under a 450-W Hanovia medium-pressure mercury lamp. Removal of the solvent under vacuum gave a residual solid, which was recrystallized from a mixture (1:1) of benzene and *n*-hexane to give 350 mg (88%) of 8c,8d-dibenzoyl-4b,8b,8c,8d-tetrahydrodibenzo[*a,f*]cyclopropa[*c,d*]pentalene (17): mp 188 °C; IR ν_{max} (KBr) 3065, 3015 and 2955 (CH), 1675 and 1665 (C=O), 1595 and 1580 (C=C) cm^{-1}; UV λ_{max} (ethanol) 230 nm (ϵ 25 000), 250 (29 500), 279 (7600), 324 (700); ^{1}H NMR ($CDCl_3$) δ 4.24 (1 H, s, methine proton), 4.64 (1 H, s, tertiary proton at 4b), 7.26 (18 H, m, aromatic); ^{13}C NMR ($CDCl_3$) δ 49.26 (C-8b), 58.19 (C-4b), 64.58 (C-8c), 74.59 (C-8d), 121.56, 121.89, 125.65, 126.14, 127.01, 127.20, 127.29, 127.69, 127.94, 128.47, 128.59, 130.02, 132.68, 133.18, 135.35, 135.57, 136.78, 137.09, 149.77, 150.51, 194.25 (carbonyl carbon), 196.76 (carbonyl carbon); mass spectrum, *m/e* (relative intensity) 412 (M$^+$, 62), 307 (55), 279 (60), 278 (30), 277 (13), 272 (12), 229 (16), 202 (36), 201 (10), 200 (13), 105 (100), 78 (55), 77 (45), 76 (15), 52 (29), 51 (30).

Anal. Calcd for $C_{30}H_{20}O_2$: C, 87.38; H, 4.85. Found: C, 87.52; H, 5.10.

In subsequent runs, several aliquot portions of a benzene solution of 10 (4.199×10^{-3} M) were irradiated in a merry-go-round with >345-nm light source both under deaerated and oxygen-saturated conditions. The yield of 17 and the amount of unchanged 10, in each case, were estimated by gas chromatography and these results are indicated in parentheses: benzene, deaerated, 5-min irradiation (17, 6.9%; 10, 92.6%); deaerated, 15-min irradiation (17, 28.7%; 10, 69.1%); deaerated, 30-min irradiation (17, 53.7%; 10, 43.9%); oxygen-saturated, 15-min irradiation (17, 3.1%; 10, 96.8%); oxygen-saturation, 30-min irradiation (17, 9.2%; 10, 86.8%).

In a separate experiment, a solution of 10 (533 mg, 1.29 mmol) in methanol (470 mL) was irradiated for 30 min with a 450-W Hanovia medium-pressure mercury lamp, and this experiment was repeated several times to irradiate, in all, 1.6 g (3.88 mmol) of 10. Removal of the solvent under vacuum gave residual solid, which was treated with a 2% solution of aqueous sodium bicarbonate (9 mL), and acidification of the bicarbonate extract with dilute hydrochloric acid (5%) gave 40 mg (8%) of benzoic acid, mp 122 °C (mixture melting point), after recrystallization from a mixture (1:9) of benzene and petroleum ether. The residue that was left behind after bicarbonate treatment was chromatographed over silica gel. Elution with a mixture (1:9) of benzene and petroleum ether gave 843 mg (52%) of 17, mp 188 °C (mixture melting point). Further elution with a mixture (1:4) of benzene and petroleum ether gave 500 mg (32%) of the unchanged starting material (10), mp 212 °C (mixture melting point), after recrystallization from acetone.

In a repeat run, a solution of 10 (500 mg, 1.2 mmol) in methanol (500 mL) was irradiated under oxygen bubbling for 30 min. Workup of the mixture as in the earlier case gave 32 mg (22%) of benzoic acid, mp 122 °C (mixture melting point), 235 mg (47%) of 17, mp 188 °C (mixture melting point), and 104 mg (21%) of the unchanged starting material (10), mp 212 °C (mixture melting point).

In a subsequent run, a solution of 10 (200 mg, 0.48 mmol) in acetone was irradiated for 30 min and workup as in the earlier cases gave 178 mg (89%) of 17, mp 188 °C (mixture melting point).

Hydrogenation of 8c,8d-Dibenzoyl-4b,8b,8c,8d-tetrahydrodibenzo[*a,f*]cyclopropa[*c,d*]pentalene (17). A mixture of 17 (412 mg, 1 mmol) and 5% Pd on charcoal (350 mg) in THF (20 mL) was hydrogenated at 10 psi for 2 h. After filtering off the catalyst, the solvent was removed under vacuum and the residue was recrystallized from acetone to give 250 mg (60%) of 9a,10-dibenzoyl-4b,9,9a,10-tetrahydro-*cis*-indeno[1,2-*a*]indene (21): mp 228–229 °C; IR ν_{max} (KBr) 3060, 3020 and 2950 (CH), 1690 (C=O), 1610 and 1590 (C=C) cm^{-1}; UV λ_{max} (methanol) 250 nm (ϵ 27600), 290 (2900, sh); ^{13}C NMR ($CDCl_3$) δ 44.33 (C-8b), 59.30 (C-4b), 62.87 (C-8d), 70.03 (C-8c), 123.97, 124.50, 125.12, 125.68, 127.04, 127.10, 127.66, 128.25, 128.34, 128.62, 128.84, 131.79, 133.18, 136.47, 136.84, 138.67, 139.66, 143.94, 145.46, 198.87 (carbonyl carbon), 200.76 (carbonyl carbon).

Anal. Calcd for $C_{30}H_{22}O_2$: C, 86.95; H, 5.31. Found: C, 87.38; H, 4.88.

Irradiation of 11,12-Dibenzoyl-9,10-dihydro-9-methyl-9,10-ethenoanthracene (11). A solution of 11 (1.8 g, 4.22 mmol) in benzene (2000 mL) was irradiated for 30 min in three lots with a 450-W Hanovia medium-pressure mercury lamp. Removal of the solvent under vacuum gave a residual solid, which was treated with a 2% solution of sodium bicarbonate. Acidification of the bicarbonate extract with dilute hydrochloric acid gave 65 mg (12%) of benzoic acid, mp 122 °C (mixture melting point), after recrystallization from a mixture (1:9) of benzene and petroleum ether. The residue that was left behind after bicarbonate treatment was chromatographed over silica gel. Elution with a mixture (1:4) of benzene and petroleum ether gave 980 mg (54%) of 8c,8d-dibenzoyl-4b,8b,8c,8d-tetrahydro-4b-methyldibenzo[*a,f*]cyclopropa[*c,d*]pentalene (18): mp 193 °C, after recrystallization from a mixture (9:1) of methanol and methylene chloride; IR ν_{max} (KBr) 3065 and 2925 (CH), 1685 and 1670 (C=O), 1605 and 1585 (C=C) cm^{-1}; UV λ_{max} (methanol) 251 nm (ϵ 28 300), 275 (7800, sh), 300 (1400, sh); ^{1}H NMR ($CDCl_3$) δ 1.74 (3 H, s, methyl protons at the C-4b position), 4.62 (1 H, s, methine proton of the cyclopropane ring), 7.30 (18 H, m, aromatic); ^{13}C NMR ($CDCl_3$) δ 16.15 (methyl carbon) 48.52 (C-8b), 59.22 (C-4b), 61.22 (C-8c), 119.73, 125.41, 126.41, 126.70, 127.23, 127.41, 127.93, 128.11, 128.27, 128.94, 129.79, 132.47, 133.01, 134.50, 134.52, 137.27, 137.67, 152.73, 153.37, 194.29 (carbonyl carbon), 195.99 (carbonyl carbon); mass spectrum, *m/e* (relative intensity) 426 (M$^+$, 52), 321 (66), 293 (35), 276 (28), 243 (13), 215 (19), 201 (10), 200 (11), 105 (100), 97 (12), 95 (10), 85 (12), 83 (15), 81 (13), 77 (68), 71 (25), 69 (25), 57 (18), 55 (34), 51 (14).

Anal. Calcd for $C_{31}H_{22}O_2$: C, 87.55; H, 5.16. Found: C, 87.42; H, 5.11.

In subsequent experiments, aliquot portions of benzene (9.7×10^{-3} M) and acetone (8.349×10^{-3} M) solutions of 11 were separately irradiated in a merry-go-round with >345-nm light source, both under deaerated and oxygen-saturation conditions. The yield of 18 and the amount of unchanged starting material (11) recovered in each case were estimated gas chromatographically and these results are indicated in parentheses: benzene, deaerated, 15-min irradiation (18, 59.5%; 11, 23.0%); benzene, deaerated, 30-min irradiation (18, 71.6%; 11, 5.0%); benzene, oxygen-saturated, 15-min irradiation (18, 7.6%; 11, 88.9%); benzene, oxygen-saturated, 30-min irradiation (18, 19.5%; 11, 69.9%); acetone, deaerated, 15-min irradiation (18, 36.9%; 11, 43.6%); acetone, deaerated, 30-min irradiation (18, 54.4%; 11, 16.3%).

In a separate experiment, a solution of 11 (1.8 g, 4.22 mmol) in methanol (1800 mL) was irradiated under a 450-W Hanovia medium-pressure mercury lamp for 30 min in three lots. Workup of the reaction mixture by removal of the solvent under vacuum gave a residue, which was treated with sodium bicarbonate solution, and on acidification with dilute hydrochloric acid gave 40 mg (8%) of benzoic acid, mp 122 °C (mixture melting point). Workup of the residue left behind, after treatment with bicarbonate, by chromatographing over silica gel and elution with a mixture (1:4) of benzene and petroleum ether gave 900 mg (50%) of 18, mp 193 °C (mixture melting point), after recrystallization from acetone. Further elution with a mixture (3:7) of benzene

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and petroleum ether gave 340 mg (19%) of the unchanged starting material (11), mp 181 °C (mixture melting point).

Hydrogenation of 8c,8d-Dibenzoyl-4b,8b,8c,8d-tetrahydro-4b-methyldibenzo[*a*,*b*]cyclopropa[*c*,*d*]pentalene (18). To a solution of 18 (426 mg, 1 mmol) in THF (20 mL) was added 400 mg of 5% palladium on charcoal and the mixture was hydrogenated at 10 psi for 2 h. After the catalyst was filtered, the solvent was removed under vacuum to give a product, which on subsequent purification through preparative thin-layer chromatography gave 9a,10-dibenzoyl-4b,9,9a,10-tetrahydro-4b-methyl-*cis*-indeno[1,2-*a*]indene (22): mp 213 °C; IR ν_{max} (KBr) 3060, 3020, 2960 and 2920 (CH), 1680 (C=O), 1600 and 1580 (C=C) cm^{-1}; UV λ_{max} (methanol) 245 nm (ϵ 23 500), 285 (3100).

Anal. Calcd for $C_{31}H_{24}O_2$: C, 86.91; H, 5.60. Found: C, 86.50; H, 4.93.

Irradiation of 11,12-Dibenzoyl-9,10-dihydro-9,10-dimethyl-9,10-ethenoanthracene (23). A. In Benzene. A solution of 23 (1.1 g, 2.5 mmol) in benzene was irradiated for 30 min, in two equal lots, under an RPR (3500 Å) light source. Removal of the solvent under vacuum gave a residual solid, which was recrystallized from methylene chloride to give 500 mg (45%) of the isomeric hydroxy derivative 29: mp 180–181 °C; IR ν_{max} (KBr) 3530 (OH), 3060, 3030, 3010, 2960 and 2920 (CH), 1650 and 1600 (C=C) cm^{-1}; UV λ_{max} (methanol) 255 nm (ϵ 24 600); mass spectrum, *m/e* (relative intensity) 440 (M$^+$, 56), 335 (58), 320 (29), 319 (41), 291 (12), 290 (15), 288 (25), 230 (29), 216 (47), 207 (50), 206 (25), 203 (13), 192 (28), 179 (51), 177 (18), 166 (30), 153 (19), 129 (21), 128 (17), 127 (23), 115 (53), 105 (100), 91 (29), 77 (68).

Anal. Calcd for $C_{32}H_{24}O_2$: C, 87.27; H, 5.45. Found: C, 87.50; H, 5.17.

The mother liquor, after the removal of 29, was extracted with an aqueous solution of sodium bicarbonate (2%). Acidification of the bicarbonate extract with dilute hydrochloric acid gave 20 mg (7%) of benzoic acid, mp 122 °C (mixture melting point). The organic layer, after extraction with bicarbonate solution, was concentrated under vacuum and subsequently chromatographed over silica gel. Elution of the column with a mixture (1:19) of benzene and petroleum ether gave 130 mg (12%) of 2,3-dibenzoyl-2,3-dihydro-1,4-dimethyl-2,3-benzonaphthalene (27): mp 154–155 °C, after recrystallization from cyclohexane; IR ν_{max} (KBr) 3053, 2977 and 2927 (CH), 1663 (C=O), 1590 and 1570 (C=C) cm^{-1}; UV λ_{max} (methanol) 243 nm (ϵ 29 000), 313 (18 000), 335 (11 500, sh); mass spectrum, *m/e* (relative intensity) 440 (M$^+$, 100), 320 (97), 231 (25), 230 (90), 228 (45), 226 (35), 215 (98), 213 (18), 202 (10), 105 (98), 78 (50), 77 (83), 62 (21), 57 (20), 55 (18), 52 (22), 51 (30).

Anal. Calcd for $C_{32}H_{24}O_2$: C, 87.27; H, 5.45. Found: C, 87.60; H, 5.10.

Further elution of the column with a mixture (3:7) of benzene and petroleum ether gave 300 mg (27%) of 1,4-dibenzoyl-5,8-dimethyl-2,3:6,7-dibenzocyclooctatetraene (24): mp 211–212 °C, after recrystallization from acetone; IR ν_{max} (KBr) 3060 and 2970 (CH), 1652 (C=O), 1605 and 1585 (C=C) cm^{-1}; UV λ_{max} (methanol) 250 nm (ϵ 3600), 282 (8100 sh); mass spectrum, *m/e* (relative intensity) 440 (M$^+$, 11), 319 (12), 230 (12), 228 (10), 215 (20), 111 (12), 109 (10), 105 (100), 97 (21), 95 (17), 85 (25), 83 (30), 81 (25), 77 (49), 71 (43), 69 (39), 67 (17), 57 (56), 43 (31).

Anal. Calcd for $C_{32}H_{24}O_2$: C, 87.27; H, 5.45. Found: C, 87.48; H, 5.38.

B. In Methanol. A solution of 23 (1.10 g, 2.5 mmol) in methanol (1000 mL) was irradiated for 15 min in two lots with a 450-W Hanovia medium-pressure lamp. Removal of the solvent under vacuum gave a residual solid, which was extracted with aqueous sodium bicarbonate solution (2%). Acidification of the bicarbonate extract gave 25 mg (8%) of benzoic acid, mp 122 °C (mixture melting point). The material that was left behind, after extraction with sodium bicarbonate, was chromatographed over silica gel. Elution with a mixture (1:1) of benzene and petroleum ether gave 275 mg (25%) of 27, mp 154–155 °C (mixture melting point), after recrystallization from cyclohexane.

Further elution of the column with a mixture (3:7) of benzene and petroleum ether gave 297 mg (27%) of 24, mp 210–211 °C (mixture melting point), after recrystallization from acetone.

Subsequent elution of the column with a mixture (1:1) of benzene and petroleum ether gave 70 mg (17%) of the unchanged starting material (23), mp 261–262 °C (mixture melting point).

Irradiation of 1,4-Dibenzoyl-5,8-dimethyl-2,3:6,7-dibenzocyclooctatetraene (24). A solution of 24 (110 mg, 0.25 (mmol) in methanol (150 mL) was irradiated for 15 min with a 450-W Hanovia medium-pressure lamp. Removal of the solvent under vacuum gave a residual solid, which was chromatographed over silica gel. Elution with a mixture (1:19) of benzene and petroleum ether gave 22 mg (20%) of 27, mp 154 °C (mixture melting point), after recrystallization from cyclohexane.

Further elution of the column with a mixture (1:9) of benzene and petroleum ether gave 36 mg (33%) of the unchanged starting material (24), mp 210–211 °C (mixture melting point).

Laser Flash Photolysis. The laser flash photolysis experiments were carried out at 337.1 nm (2–3 mJ, $\sim$8 ns) in a computer-controlled set-up with a Molectron UV-400 nitrogen laser system. The system is fully interphased with a PDP 11/55 multiuser computer which controls the experiment, averages signals, and processes the data. The instrument allows the monitoring of transient phenomena in the 10 ns–100 μs time range. Details of the apparatus and the procedures are described elsewhere.[24] Unless otherwise mentioned, the solutions used in all experiments were deaerated by purging with oxygen-free argon.

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