Photochemical and Thermal Transformations of 2(3*H*)-Furanones and Bis(benzofuranones). A Laser Flash Photolysis Study[1]

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Abstract: Transformations of the 2(3*H*)-furanones **1–4** and bis(benzofuranones) **16–18** under steady-state photolysis and thermolysis are reported. Irradiation of **1** in benzene gives a mixture of the decarbonylated product **5** (62%) and the cyclized phenanthene derivative **10** (15%). Similar results were obtained when the photolysis of **1** was carried out in methanol and acetone. Irradiation of **2** in benzene and methanol gave exclusively the decarbonylation product **6**, whereas, in acetone, a mixture of the rearranged lactone **13** and its cyclized product, **15**, was obtained. Irradiations of both **3** and **4** gave the cyclized products **11** and **12**, respectively. In contrast, the photolysis of the bis(benzofuranone) **16** in cyclohexane gave 3-phenylbenzo[*b*]-2-(3*H*)-furanone (**25**), whereas the photolysis in methanol led to a mixture of methyl α-(2-hydroxyphenyl)phenylacetate (**34**) and 3-hydroxy-3-phenylbenzo[*b*]-2(3*H*)-furanone (**31**). Similar results were obtained in the irradiation of **17** and **18**. Neat thermolysis of furanones **1–3** at 350–450 °C gave the decarbonylated products **5**, **6**, and **37** in 36–80% yields, whereas furanone **4** underwent facile isomerization to 5-benzyl-3,4,5-triphenyl-2(5*H*)-furanone (**38**), upon refluxing in diphenyl ether (~255 °C). Heating of bis(benzofuranones) **16–18** in refluxing cumene (~150 °C) gave the corresponding furanones **25–27** in 62–68% yields. Laser flash photolysis of furanones **1–4** at 248 and 337 nm leads to absorption spectral changes that can be explained in terms of singlet-mediated decarbonylation ($\phi = 0.3$ for **2** in methanol, $\lambda_{ex} = 248$ nm) and cyclization, i.e., dihydrophenanthrene formation ($\phi = 0.1$–0.5 for **1**, **3**, and **4** in benzene and methanol, $\lambda_{ex} = 337$ nm). The triplets of the furanones generated under energy-transfer sensitization by benzophenone in benzene are relatively long lived ($\tau = 1.2$–$12\ \mu$s) and exhibit absorption maxima at 330–370 nm ($\epsilon_{max} = (11$–$14) \times 10^3$ M^{-1} cm^{-1}); these spectral and kinetic features appear to be characteristic of the styrene and *cis*-stilbene chromophores, constrained into planar configurations. Upon laser flash photolysis at 248 nm in methanol, bis(benzofuranones) **16–18** undergo facile fragmentation to the corresponding radicals **19–21**, characterized by sharp and intense absorption maxima at ~330 nm, in addition to broad and weak absorption band systems at 500–600 nm; these radical species are the primary intermediates implicated in the formation of various final products in the course of steady-state photolysis of **16–18** under different conditions.

Photochemical and thermal transformations of several unsaturated lactones such as 2(3*H*)-furanones and 2(5*H*)-furanones have been investigated in detail.[3] Some of the prominent photoreaction pathways of unsaturated lactones include decarbonylation,[3b,c,g,4] decarboxylation,[3d] solvent addition to double bonds,[3h,j,n,p] migration of aryl substituents,[3p] and dimerization.[3k] In the case of 2(3*H*)-furanones, for example, it has been suggested that one of the critical requirements for decarbonylation of these compounds is the initial cleavage of the acyl–oxygen bond leading to stabilized diradical intermediates, which can subsequently lose carbon monoxide, leading to α,β-unsaturated ketones.[3g] Similar photochemical decarbonylation reactions have been observed in several related systems.[5-9]

Besides decarbonylation, dimerization and the formation of chromone derivatives have also been observed in the case of 2-(3*H*)-furanones.[3r,10] Padwa and co-workers[11-13] have shown that the phototransformations of benzo[*b*]-2(3*H*)-furanones lead to a variety of products, arising through quinone methide intermediates.

In contrast to the photochemical transformations of 2(3*H*)-furanones, the thermal transformations of these substrates lead to decarbonylation products[3s,t] and, in some cases, rearrangement products, arising through a [1,3]-sigmatropic shift of the substituent groups.[3u,14] The thermal transformations of bis(benzofuranones), on the other hand, are known to give rise to a variety of products, arising through radical intermediates.[15,16]

In the present study, photochemical and thermal transformations of a few 2(3*H*)-furanones and bis(benzofuranones) were investigated in detail. Laser flash photolysis technique was employed for the first time to examine the mechanistic aspects of these photochemical reactions. Furthermore, spectral and kinetic data were obtained for the triplets of 2(3*H*)-furanones containing styrene and *cis*-stilbene moieties constrained into planar geometries. The 2(3*H*)-furanones that we have examined include

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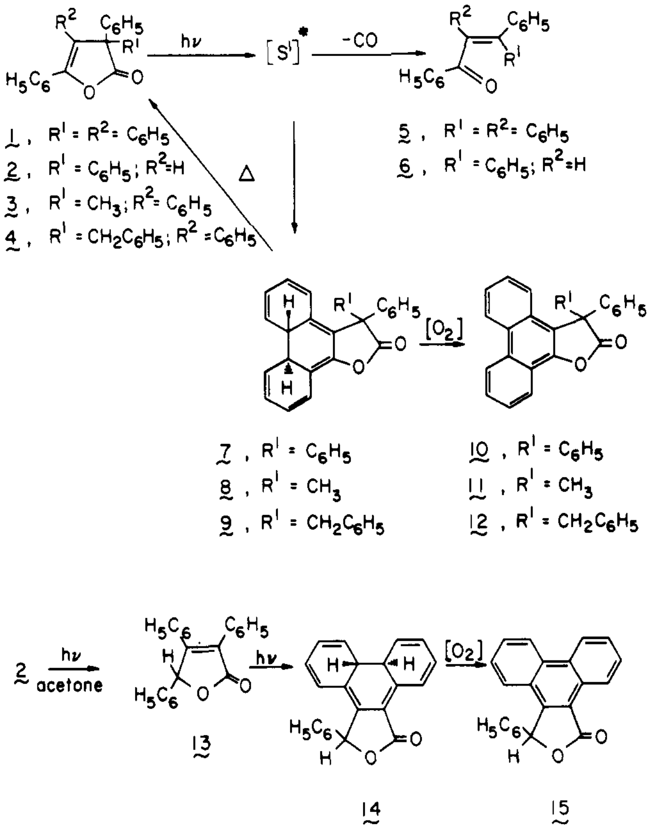
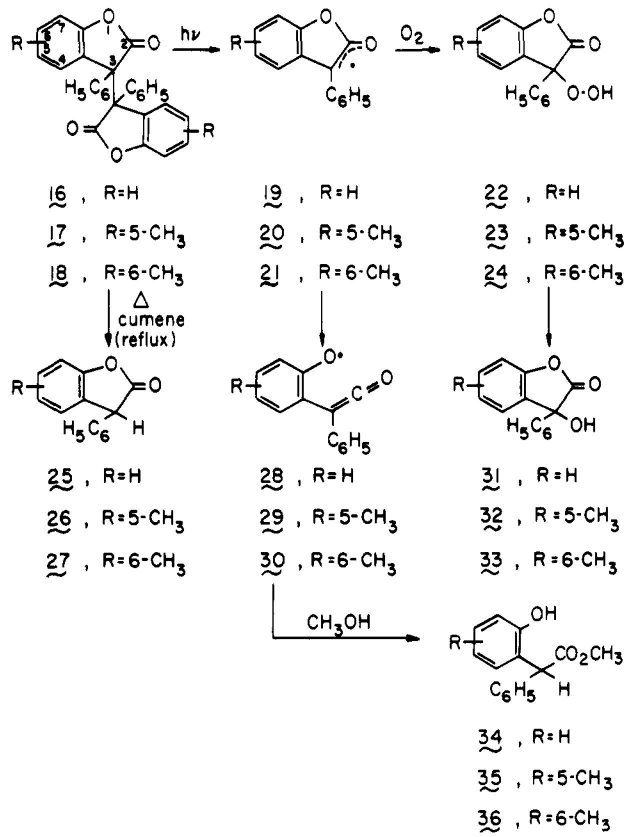
Scheme I



Scheme II



3,3,4,5-tetraphenyl-2(3*H*)-furanone (**1**), 3,3,5-triphenyl-2(3*H*)-furanone (**2**), 3-methyl-3,4,5-triphenyl-2(3*H*)-furanone (**3**), and 3-benzyl-3,4,5-triphenyl-2(3*H*)-furanone (**4**), whereas the bisbenzofuranones include 3,3′-diphenyl-3,3′-dibenzo[*b*]furan-2,2′-(3*H*,3′*H*)-dione (**16**), 5,5′-dimethyl-3,3′-diphenyl-3,3′-bibenzo[*b*]furan-2,2′(3*H*,3′*H*)-dione (**17**), and 6,6′-dimethyl-3,3′-diphenyl-3,3′-dibenzo[*b*]furan-2,2′(3*H*,3′*H*)-dione (**18**).

Results

1. Preparative Photochemistry and Product Identification. 1.1. Photochemical Transformations of 2(3*H*)-Furanones (1–4). Photolysis of a solution of the 2(3*H*)-furanone **1** in benzene or methanol gave a mixture of 3,3-diphenylphenanthro[9,10-*b*]furan-2(3*H*)-one (**10**, 15–17%) and 1,2,3,3-tetraphenylprop-2-en-1-one (**5**, 62–66%). When the irradiation was carried out in methanol under oxygen saturation, the yield of cyclization product **10** increased to 32%. On the other hand, irradiation of **1** in acetone led to only the decarbonylated product **5** (42%).

Similarly, irradiation of the furanone **2** in benzene and methanol gave rise to only the decarbonylation product 1,3,3-triphenylprop-2-en-1-one (**6**),[3s,t] in 87% and 66% yields, respectively. In contrast, a 15% yield of a rearranged product, 3,4,5-triphenyl-2(5*H*)-furanone (**13**) and 3-phenylphenanthro[9,10-*c*]furan-1-(3*H*)-one (**15**) (65%) were obtained (Scheme I),[3e,f] when irradiation of **2** was carried out in acetone. Irradiation of the rearranged product **13** in benzene, under oxygen saturation gave a 82% yield of **15**.

Photolysis of **3** in benzene and methanol gave the corresponding cyclization product 3-methyl-3-phenylphenanthro[9,10-*b*]furan-2(3*H*)-one (**11**), in 11% and 19% yields, respectively; large quantities of the unchanged starting material were recovered in each case. On the other hand, when the irradiation of **3** was conducted in oxygen-saturated solutions, the yield of **11** increased to 55–58%. Irradiation of **3** in acetone, however, did not give rise to any product; only the starting material could be recovered unchanged.

Similarly, the irradiation of **4** in benzene and methanol gave the corresponding cyclized product, 3-benzyl-3-phenylphenanthro[9,10-*b*]furan-2(3*H*)-one (**12**) in 70% and 69% yields, respectively. However, the yield of **12** was increased to 87–90%, when the irradiation was carried out under oxygen saturation. Likewise, the photolysis of **4** in acetone gave a 50% yield of **12**, along with some unreacted starting material. The structures of the photoproducts **10–12** have been deduced from analytical results and spectral data (see Experimental Section).

1.2. Photochemical Transformations of Bis(benzofuranones) 16–18. The photolysis of **16** in benzene did not yield any product; however, when the irradiation of **16** was carried out in cyclohexane, a 12% yield of 3-phenylbenzo[*b*]-2(3*H*)-furanone (**25**) was obtained. The irradiation of **16** in methanol gave a mixture of methyl α-(2-hydroxyphenyl)phenylacetate (**34**, 10%)[17] and 3-hydroxy-3-phenylbenzo[*b*]-2(3*H*)-furanone (**31**, 40%)[13] (Scheme II).

Similarly, the irradiation of **17** in benzene did not give rise to any photoproduct, whereas the irradiation in methanol gave a 18% yield of methyl α-(2-hydroxy-5-methylphenyl)phenylacetate (**35**) and a 25% yield of 3-hydroxy-5-methyl-3-phenylbenzo[*b*]-2-(3*H*)-furanone (**32**). Likewise, when the irradiation of **18** was carried out in benzene no photoproduct was observed, whereas the irradiation in methanol gave a mixture of methyl α-(2-hydroxy-4-methylphenyl)phenylacetate (**36**, 11%) and 3-hydroxy-6-methyl-3-phenylbenzo[*b*]-2(3*H*)-furanone (**33**, 37%). The lack of reactivity of **16–18** in benzene is attributed to the fact that the solvent screens most of the light under these conditions (see Experimental Section). The structures of **32**, **33**, **35**, and **36** have been assigned on the basis of analytical results and spectral data.

2. Thermal Transformations of 2(3*H*)-Furanones 1–4 and Bis(benzofuranones) 16–18. Thermolysis of **1** in refluxing diphenyl ether (~255 °C) did not lead to any product, whereas, when it was heated at 350 °C, **1** underwent decarbonylation to give a 40% yield of **5**. On the other hand, thermolysis of **1** at 450 °C resulted in a 80% yield of **5**. Similarly, the thermolysis of **2** at 350 °C gave a 55% yield of **6**, whereas the heating of **2** at 450 °C gave a 82% yield of **6**. Furanone **3** underwent decarbonylation at 310 °C to give a 36% yield of **37**, and a small amount (9%) of benzoic

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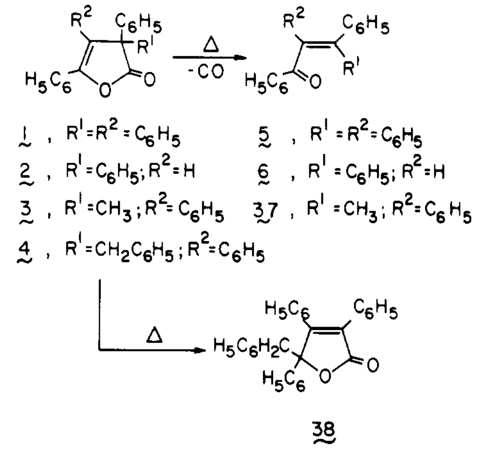
Scheme III



acid. In contrast, furanone **4** on refluxing in diphenyl ether gave the isomeric product, 5-benzyl-3,4,5-triphenyl-2(5*H*)-furanone (**38**, 95%) (Scheme III).

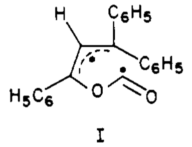
The formation of the decarbonylation products **5**, **6**, and **37** in the thermolysis of **1**, **2**, and **3**, respectively, could be understood in terms of a symmetry-allowed, cheletropic reaction[3i,14] or through a stepwise process invlving diradical intermediates. The formation of the rearranged product **38**, in the thermolysis of **4**, may be via a thermal [1,3]-sigmatropic shift with inversion of configuration at the migrating center[14] or through radical pathways (Scheme III).

In contrast to furanones, the bis(benzofuranones) undergo homolysis on heating. Thus, refluxing of **16** in diphenyl ether ($\sim$255 °C) gave a 42% yield of **25**; whereas in refluxing cumene ($\sim$150 °C), a 68% yield of **25** was obtained. Similarly, the bis(benzofuranones) **17** and **18** in refluxing cumene gave the corresponding furanones **26** and **27** in 65% and 62% yields, respectively (Scheme II).

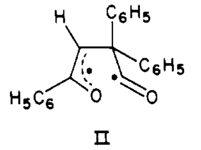
The formation of the furanones **25**, **26**, and **27** from **16**, **17**, and **18**, respectively, can be understood in terms of the initial homolytic cleavage leading to the radical intermediates **19**–**21**[16] (Scheme II). These radicals (**19**–**21**) can subsequently abstract hydrogen atoms from the solvent to give the furanones **25**, **26**, and **27**, respectively.

3. Laser Flash Photolysis Studies. The laser flash photolysis experiments were carried out with excitation by pulses from a nitrogen laser (337.1 nm, 8 ns, 3 mJ) and/or a Kr–F_2 excimer laser (248 nm, 20 ns, 10–20 mJ). The latter wavelength was particularly suitable for direct excitatin of the furanone **2**, which absorbs very little at the longer wavelength (337.1 nm). On the other hand, the 337.1-nm laser pulses could be conveniently used in triplet sensitization experiments that required preferential excitation of the donor, benzophenone. Transient phenomena in the time domain of 100 ns to 100 μs were observed in terms of spectral absorption in the region 280–700 nm.

3.1. Direct Excitation of 2(3*H*)-Furanones 1–4. Upon 248-nm laser flash photolysis in methanol, furanone **2** produces a long-lived photoproduct absorbing at short wavelengths, 280–350 nm (λ_{max} = 310 nm, see Figure 1A); the formation of this species becomes complete within the laser pulse and it shows no sign of decay over $\sim$100 μs in the absence or presence of oxygen in the solution. This "permanent" photoproduct is assigned as the α,β-unsaturated ketone **6**, formed in the ground state via decarbonylation, on the basis of the fact that the observed spectrum agrees very well with the difference absorption spectrum of the α,β-unsaturated ketone **6** and the parent furanone **2** (Figure 1A). Alternative assignments in terms of diradical species I or II, formed by initial cleavage of either of the bonds to the carbonyl group, are ruled out by the "permanent" nature of the absorbance change as well as its insensitivity toward oxygen. Furthermore, in analogy to diphenylhydroxymethyl and diphenylmethyl radicals,[18-20] one would expect a lower intensity broad-band system for I in the visible region; this is not observed in the spectrum derived from photolysis of **2**.



I



II

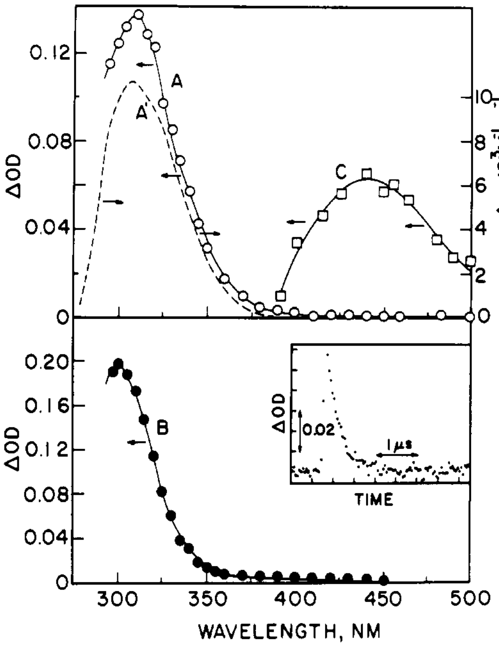


Figure 1. Absorption spectra of the photoproduct observed upon 248-nm laser flash photolysis of furanone **2** in (A) methanol and (B) cyclohexane. The broken curve A′ is the difference absorption spectrum of **6** and **2**. C is the transient absorption spectrum due to the triplet of **6** in methanol, obtained by 337.1-nm excitation of **6** and monitored at 100 ns following the laser pulse. An experimental decay profile of the triplet of **6** monitored at 440 nm in degassed methanol is shown in the inset.

The absorbance change at 310 nm due to the "permanent" photoproduct is found to be linearly related with the laser intensity, suggesting that the decarbonylation process is monophotonic. Using naphthalene in cyclohexane as an actinometer (ϕ_T = 0.75)[21] and comparing the absorbance due to naphthalene triplet at 414 nm (ϵ_{max} = 24.5 × 10^3 M^{-1} cm^{-1})[21] with that due to the photoproduct at 310 nm observed in solutions optically matched at 248 nm, we estimated the quantum yield of photoelimination of CO at 0.3 ± 0.1 (in degassed methanol).

Interestingly, in the course of 248-nm laser flash photolysis of furanone **2** in degassed methanol, a relatively short-lived transient species (τ = 325 nm) is also formed in small yields. This species absorbs at 400–480 nm (λ_{max} = 440 nm) and is assigned as the triplet of the photoproduct **6** on the basis of the fact that a transient species with identical spectral features and oxygen sensitivity is also formed upon direct 337.1-nm laser photolysis of the latter. It is noted that the observed lifetime (325 ns), though short, is much longer than τ_T's recently reported for the triplets of various chalcones (5–29 ns in methanol).[22] The mechanism of the formation of the photoproduct in the excited state (triplet) is not quite well understood. A study of the laser intensity dependence shows that the yiled of the triplet increases supralinearly with increase in laser intensity; thus, a trivial cause of its formation could be the excitation of **6** formed during the same exciting laser pulse. No reliable quantitative analysis of this aspect was feasible because of the low level of signals due to the triplet absorption.

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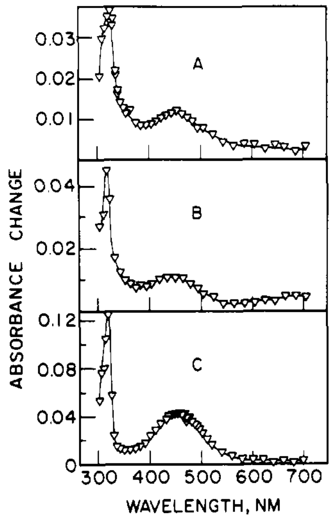

Figure 2. Transient absorption spectra observed at ~5 μs following 248-nm laser flash photolysis of furanones **1** (A), **3** (B), and **4** (C) in methanol.

In cyclohexane, furanone **2** showed transient phenomena (Figure 1B) very similar to those in methanol (described above). The lifetime of the triplet of **6** in cyclohexane is 350 ns. The 248-nm laser excitation of furanones **1**, **3**, and **4** in methanol results not only in sharp, strong, and long-lived absorption spectral changes at short wavelengths (300–350 nm) but also in the formation of a major species that absorbs in the visible, namely, 420–500 nm (λ_{max} = 450–470 nm). The transient spectra in degassed methanol are presented in Figure 2A–C. Under the conditions of our experiments, the extent of the decay of the 450–470-nm species over ~100 μs was found to be very small (≤10%).[23]

In view of the presence of vicinal phenyl groups in cis configuration at 4- and 5-positions in each of the furanones **1**, **3**, and **4** and the fact that phenanthrene derivatives are isolated as major photoproducts in the course of steady-state irradiation of these substrates, it is reasonable to identify the long-lived transients absorbing at 400–500 nm as the products of photocyclization, namely, dihydrophenanthrenes **7–9**. This is supported by the similarity of the transient spectra and kinetic behaviors observed in the present cases with those of 4a,4b-dihydrophenanthrenes, produced in 248-nm laser flash photolysis[24] of *cis*-stilbene, triphenylethylene, and tetraphenylethylene as well as those generated[25] from *cis*-stilbene and diphenylcyclopentene by steady-state photolysis (280 nm) in 2:1 methylcyclohexane/isohexane mixtures at −10 °C. It is noted that the absorption spectra of 4a,4b-dihydrophenanthrenes are characterized[25] by sharp and intense band systems at 300–320 nm with extinction coefficients about 3 times higher than those of the band systems at 450 nm. Thus, the transient absorption observed at short wavelengths (300–330 nm) in the spectra in Figure 2A–C is primarily due to the dihydrophenanthrenes.

Table I. Data regarding Absorption Maxima and Quantum Yields of Formation of Dihydrophenanthrenes

furanone	solvent	λ_{max}[a]	ϕ_{DHP}[b]
1	benzene	450	0.1
	methanol	455	0.09
3	benzene	450	0.1
	methanol	450	0.1
4	benzene	465	0.5
	methanol	470	0.4

[a] ±5 nm. [b] ±20%; calculated with the assumption that the extinction coefficients of the dihydrophenanthrenes are all 6.8 × 10^3 M^{-1} cm^{-1} at the respective maxima (see text).

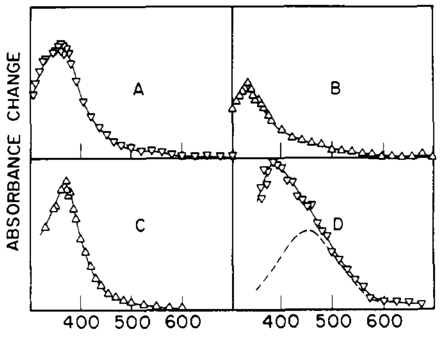

Figure 3. Transient absorption spectra, A–D, of the triplet of furanones **1–4** produced by energy transfer from benzophenone in benzene (λ_{ex} = 337.1 nm). The dotted curve in D is the spectrum due to dihydrophenanthrene photoproduct monitored after the completion of the triplet decay; this is formed because of partial absorption of the laser photons by furanone **4** (2 mM) under the conditions of the experiment.

The lowest energy absorption-band systems of furanones **1**, **3**, and **4** occupy the spectral region 250–350 nm (λ_{max} (nm) = 279, 274, and 290 and ϵ_{max} (10^3 M^{-1} cm^{-1}) = 9.1, 10.4, and 8.6, respectively, in methanol). Although the absorption at 337.1 nm is weak (ϵ = 130–750 M^{-1} cm^{-1}), it was possible to carry out laser flash photolysis of these furanones at this wavelength by using relatively concentrated solutions. The transient absorption spectra under 337.1-nm excitation in benzene and methanol were very similar to those under 248-nm excitation in methanol. We have estimated the quantum yields (ϕ_{DHP}) of dihydrophenanthrene formation (with λ_{ex} = 337.1 nm) assuming that their maximum extinction coefficients at 450–470 nm are identical with that reported[25] for 4a,4b-dihydrophenanthrene from *cis*-stilbene, i.e., 6.8 × 10^3 M^{-1} cm^{-1} in 2:1 methylcyclohexane and isohexane at −10 °C. Benzophenone triplet formation (ϕ_T = 1) in benzene was used for actinometry. The data concerning ϕ_{DHP} are given in Table I.

At the longest time scale (~100 μs) available to us, practically no enhancement of the decay of the dihydrophenanthrenes was observed in air- or oxygen-saturated solutions. This suggests that the rate constants for their reaction with oxygen leading to phenanthrene formation are small (<10^5 M^{-1} s^{-1}). On the other hand, iodine in benzene proved to be a relatively efficient quencher for the dihydrophenanthrenes (k_q ~ 10^8 M^{-1} s^{-1} for **8**).

3.2. Triplets of 2(3*H*)-Furanones 1–4: Sensitization by Benzophenone under 337.1-nm Laser Excitation. In order to establish whether the decarbnylation and cyclization reactions of the furanones occur in their singlet or triplet excited states, it was necessary to characterize their triplets by generating them indirectly under conditions of energy-transfer sensitization. The results are also of considerable interest because the furanones under consideration constitute styrene and stilbene analogues locked in planar, cisoid geometries. Since the perpendicular forms of the olefinic triplets appear to be unfavorable because of the strain imposed on the ring by the twisting about the olefinic double bond, the spectral and kinetic behaviors of the furanone triplets should shed light on the planar forms of the triplets of styrene and *cis*-stilbene.

We performed experiments in which benzophenone (0.04–0.06 M) was preferentially excited at 337.1 nm in the presence of varying concentrations (0.5–3 mM) of the furanones in benzene and the first-order decay of benzophenone triplet (donor) was followed by monitoring its spectral absorption at 532 nm. The slopes of linear plots based on eq 1 gave the bimolecular rate

$$k_{obsd} = \tau_T^{-1} + k_q^T[Q] \qquad (1)$$

constants (k_q^T) for energy transfer from benzophenone triplet to the furanones (k_{obsd} is the pseudo-first-order rate constant for the decay of benzophenone triplet in the presence of a furanone at

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(23) In the case of furanone **3**, a small transient absorption decaying with a lifetime of 3.1 μs in degassed methanol was also noticeable at 400–450 nm (λ_{max} = 440 nm); this could possibly be due to the triplet of one of the photoproducts, namely, 1,2,3-triphenylprop-2-en-1-one or the dihydrophenanthrene, **8**.

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Table II. Data concerning Furanone Triplets Produced by Energy Transfer from Benzophenone in Benzene (Deaerated)

furanone	$k_q{}^T$,[a] 10^9 (M^{-1} s^{-1})	λ_{max},[b] nm	ϵ_{max},[c] 10^3 (M^{-1} cm^{-1})	τ_T,[a] μs	k_{q,O_2},[a] 10^9 (M^{-1} s^{-1})
1	2.5	365	13	12	1.7
2	2.1	330	13	1.2	2.0
3	2.9	370	11	12	1.9
4	2.7	375	14	8.2	1.4

[a] ±15%. [b] ±5%. [c] ±20%.

concentration [Q] and τ_T is its lifetime in the absence of a quencher). The transient spectra following the completion of the decay of benzophenone triplet in the presence of 0.5–2 mM furanones are presented in Figure 3A–D. The furanone triplets are characterized by lifetimes in the range 1.2–12 μs and absorption maxima at 330–370 nm. Comparison of end-of-pulse absorbance due to benzophenone triplet at 532 nm in the absence of a quencher with the transient absorbances due to the furanone triplets under 70–95% quenching of the former by energy transfer enabled us to estimate the extinction coefficients of triplet–triplet absorption of the latter.

The data concerning spectra and decay lifetimes of furanone triplets, rate constants ($k_q{}^T$) for energy transfer to them from benzophenone, and those (k_q, O_2) for oxygen quenching are summarized in Table II. Similar spectral data for the furanones were also obtained under triplet sensitization by biphenyl triplet, produced by pulse radiolysis[26] in benzene. The spectra and maxima (365–375 nm) of the furanone triplets containing phenyl groups at both 4- and 5-positions bear resemblance to the spectrum attributed to the planar form[27] of stilbene triplet. The relatively long lifetimes (1.2–12 μs) of the furanone triplets contrasted against the very short triplet lifetimes of stilbene (~60 nm in benzene)[27] and styrenes (20–90 ns in methanol)[28] suggest that the former exist primarily in planr configurations. The oxygen-quenching rate constants ((1.4–2.0) × 10^9 M^{-1} s^{-1}) are all close to one-ninth of the rate (k_d) under diffusion control, as normally expected from spin-statistical restriction for energy-transfer quenching at the planar ethylenic configuration. In contrast, k_{q,O_2} is much higher for stilbene triplet (8.0 × 10^9 M^{-1} s^{-1} in benzene);[27] this is considered to be a manifestation of enhanced quenching via spin-exchange interaction[29] at the twisted geometry.

3.3. Direct Laser Photolysis of 3-Benzyl-3-phenylphenanthro-[9,10-*b*]-furan-2(3*H*)-one (12). Laser excitation of **12** in benzene (λ_{ex} = 337.1 nm) and methanol (λ_{ex} = 337.1 and 248 nm) leads to the formation of a transient with absorption maxima at 485–490 nm (Figure 4) and lifetimes 4–5 μs. The decay of this transient is oxygen sensitive (k_{q,O_2} ~ 6 × 10^8 M^{-1} s^{-1} in both methanol and benzene). The transient absorption spectra are very similar to the triplet–triplet absorptin of phenanthrene (λ_{max} = 493 nm in benzene).[21] Also, the transient is quenched by 1-methylnaphthalene and 2,5-dimethyl-2,4-hexadiene with rate constants (1.3 × 10^9 M^{-1} s^{-1} for both quenchers) similar to those for the quenching of phenanthrene triplet (1.9 × 10^9 and 1.7 × 10^9 M^{-1} s^{-1}, respectively). On the basis of these observations the transient species is identified as the triplet of phenanthrene chromophore in the furanone. An alternative assignment in terms of the triplet of the decarbonylated product is ruled out by the fact that the 490-nm species is also produced by energy transfer under preferential excitation of benzophenone in the presence of **12** in benzene. It should be noted that following the decay of the triplet of **12** in deaerated or air-saturated solutions, a small, residual "permanent" absorption becomes apparent at 320–350 nm; this is possibly due to the products of the photoreaction of **12**.

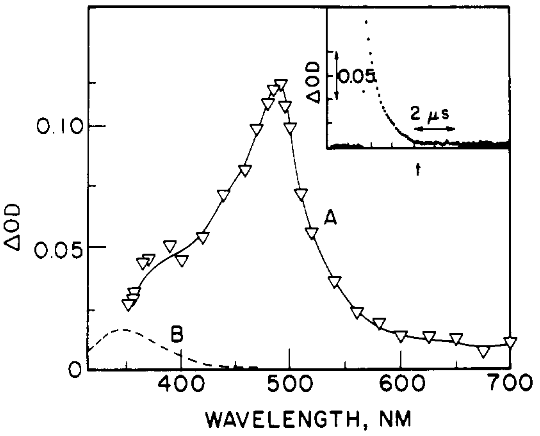

Figure 4. Transient absorption (A) observed upon 337.1-nm laser flash photolysis of **12** in air-saturated benzene at 0.4 μs following the laser flash. The broken curve B is the spectrum of residual "permanent" absorption following the decay of the transient. The inset shows an experimental decay profile at 490 nm.

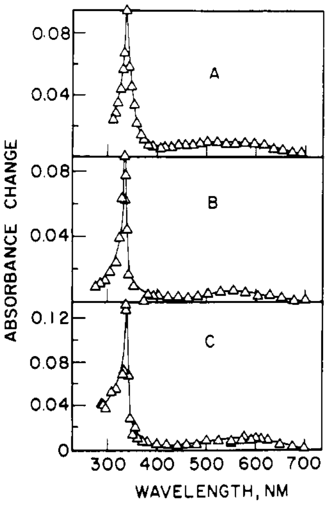

Figure 5. Transient absorption spectra, A–C, observed at ~2 μs following 248-nm laser flash photolysis of bis(benzofuranones) **16–18** in degassed methanol.

3.4. 248-nm Laser Photolysis of Bis(benzofuranones) 16–18. Upon laser flash photolysis with 248-nm pulses in methanol, the bis(benzofuranone) **16** produces a transient species characterized by a sharp and intense absorption maximum at 330 nm as well as a broad and weak absorption-band system in the visible region (450–650 nm, see Figure 5). In view of the steady-state photochemistry of bis(benzofuranones) discussed earlier as well as similarity of the spectrum with the spectra of diphenylmethyl radicals,[18-20] the most probable assignment for the transient appears to be in terms of the radical **19**, produced as a result of symmetric photocleavage. Under the conditions of our measurements, the radical undergoes ~50% decay over 80 μs and only a very slight enhancement of the decay is observed in oxygen-saturated methanol (k_{q,O_2} ≤ 10^5 M^{-1} s^{-1}).

Discussion

Pertinent to the understanding of the mechanisms of photoinduced decarbonylation and cyclization of furanones **1–4** are the facts that the transients assigned as furanone triplets (λ_{max} = 330–370 nm) are not produced to any significant extent in the course of the direct photolyses (248 or 337.1 nm) of these compounds and that no relatively slow growths of spectral absorptions attributable to triplet-mediated formation of decarbonylation and cyclization products are observed under conditions of triplet sensitization. These results establish that both of the major photoprocesses occur through the intermediacy of singlet excited states. Singlet-mediated photocyclization of diarylethylenes

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(26) For a description of the pulse-radiolytic method of generating triplets, see: (a) Bensasson, R.; Land, E. J. *Trans. Faraday Soc.* **1971**, *67*, 1904–1915. (b) Land, E. J. *Proc. R. Soc. London, Ser. A* **1968**, *A305*, 459–471.

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(including *cis*-stilbene) leading to dihydrophenanthrenes, which, in turn, are oxidized to phenanthrenes or undergo thermal reversion to the ethylenes, is well recognized in the literature.[25,30]

The formation of the various products in the phototransformations of the different 2(3*H*)-furanones **1–4** could be understood in terms of the pathway shown in Scheme I. The initial excitation of the furanones **1–4** leads to the corresponding singlet excited states, which in turn undergo chemical reactions leading either to dihydrophenanthrene derivatives **7–9** (through electrocyclic ring closure reactions) or decarbonylation products such as **5** and **6** (through one-photon, two-bond fragmentation on a subnanosecond time scale). The dihydrophenanthrenes **7–9**, in turn, undergo subsequent air oxidation under the reaction conditions to give the corresponding phenanthrene derivatives **10–12**. The fact that improved yields of **10**, **11**, and **12** have been observed when the photolyses of **1**, **3**, and **4**, respectively, are carried out under oxygen saturation confirms this assumption. The formation of the rearranged product **13** in the acetone-sensitized photoreaction of **2** would imply that the rearrangement of **2** to **13** may be proceeding from the triplet state. The laser flash photolytic observation that $\phi_T \sim 0$ for the furanones under study as well as the lack of formation of the rearranged product under direct photolysis supports this conclusion.

It is tempting to consider the relative importance of photochemical decarbonylation and cyclization in furanones **1**, **3**, and **4** in the light of the results of steady-state and laser flash photolysis. Although the ϕ_{DHP} data in Table I are meant to be semiquantitative in view of the uncertainty in the extinction coefficients of the dihydrophenanthrenes, ϕ_{DHP}'s of furanone **4** are large enough (relative to those of **1** and **3**) to imply that photocyclization is dominant in this system relative to photoelimination of CO. This is also reflected in the results of steady-state photolyses for **4**, that is, isolation of the phenanthrene derivative in very high yields and lack of the decarbonylation product. A plausible explanation for the difference in the behavior of **4** with respect to **1** may be sought in terms of the greater stability of the incipient vinyldiphenylmethyl radical formed in the initial stage of bond cleavage for the loss of CO in the case of **1**. In the case of **4** as well as **3**, the stabilization of corresponding radicals is expected to be smaller because of conjugation with only one phenyl group.

The formation of 3-hydroxy-3-phenylbenzo[*b*]-2(3*H*)-furanones **31**, **32**, and **33** and the esters **34**, **35**, and **36** in the photolysis of **16**, **17**, and **18**, respectively, can be understood in terms of the pathways shown in Scheme II. As suggested by the 248-nm laser flash photolysis of **16**, the primary process in the phototransformations of **16**, **17**, and **18** is the homolysis of the 3,3′-bond in the singlet and/or triplet excited states of these substrates to give the corresponding radical intermediates **19–21**, which in turn rearrange to the ketene radical intermediates **28–30**; the latter ultimately will lead to the esters **34–36**, through hydrogen atom abstraction from the solvent and also methanol addition. The triplet sensitization experiments in the cases of **16–18**, however, could not be carried out due to the nonavailability of suitable sensitizers with high triplet energy (≥85 kcal mol^{-1}). The formation of the hydroxybenzofuranones **31–33**, on the other hand, could be explained in terms of the hydroperoxide intermediates **22–24**, formed through the reaction of the initially formed radical intermediates **19–21** with molecular oxygen.[31] The absence of the benzofuranones **25**, **26**, and **27** or their transformation products in the photolysis of **16**, **17**, and **18**, respectively, in solvents such as methanol suggests that the hydrogen atom abstraction of the radical intermediates **19–21** may not be competing favorably in these reactions, when compared to the other two pathways shown in Scheme II. It may be pointed out, however, that a small yield (12%) of 3-phenylbenzo[*b*]-2(3*H*)-furanone (**25**) could be obtained when the photolysis of **16** was carried out in a solvent such as cyclohexane, showing thereby that, in this solvent, the hydrogen abstraction reaction of the radical intermediate **19** becomes important.

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 580 infrared spectrometers. The electronic spectra were recorded on Beckman DB, Cary 17, or Cary 219 spectrophotometers. The NMR traces were recorded on either Varian A-60 or Brucker WP-80 spectrometers, using tetramethylsilane as internal standard. The mass spectra were recorded on a Hitachi RMU-6E single focusing mass spectrometer or a Varian Mat CH7 mass spectrometer at 70 eV. Irradiations were carried out in a Srinivasan-Griffin Rayonet photochemical reactor (2537 or 3500 Å) or using a Hanovia 450-W medium-pressure mercury lamp in a quartz-jacketed immersion well.

Starting Materials. The furanones **1**,[3s,t] mp 137–138 °C, **2**,[3s,t] mp 120–121 °C, **3**,[3e] mp 118–119 °C, **4**,[32] mp 154 °C, and bis(benzofuranones **16**,[16] mp 175–176 °C, **17**,[16] mp 158 °C, and **18**,[16] mp 170–171 °C were prepared by reported procedures. Solvents for 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.

Photolysis of 3,3,4,5-Tetraphenyl-2(3*H*)-furanone (1). A solution of **1** (40 mg, 0.1 mmol) in benzene (60 mL) was irradiated for 6 h under an RPR (3500 Å) light source. Removal of the solvent under vacuum gave a residue, which was chromatographed over silica gel. Elution of the column with petroleum ether gave 5 mg (15%) of **10**, mp 220–221 °C, after recrystallization from methanol: ^{1}H NMR (CDCl$_3$) δ 7.55 (16 H, m, Ar), 8.7 (2 H, m, phenanthrene H^4 and H^5 protons); mass spectrum, *m/e* (relative intensity) 386 (M$^+$, 100), 358 (M$^+$ − CO, 63), 309 (M$^+$ − C$_6$H$_5$, 7), 281 (M$^+$ − CO, − C$_6$H$_5$, 56) and other peaks.

Continued elution of the column with a mixture (1:4) of benzene and petroleum ether gave 23 mg (62%) of **5**,[3s,t] mp 152–153 °C (mixture melting point), after recrystallization from methanol. In several repeat experiments, the photolysis of **1** was carried out in different solvents and conditions to give varying yields of products as indicated in parentheses: benzene, 6 h (RPR, 3500 Å), oxygen saturated (**10**, 33%; **5**, 28%); methanol, degassed, 6 h (RPR, 3500 Å), (**10**, 32%; **5**, 29%); acetone, degassed, 4 h (RPR, 3500 Å) (**5**, 42%; **1**, 39% (recovery)).

Photolysis of 3,3,5-Triphenyl-2(3*H*)-furanone (2). A solution of **2** (0.3 g, 1 mmol) in benzene (250 mL) was irradiated for 9 h under an RPR (2537 Å) light source. The solvent was removed under vacuum, and the residue thus obtained was recrystallized from methanol to give 240 mg (87%) of **6**,[3s,t] mp 92 °C (mixture melting point). In a repeat run, a solution of **2** (0.2 g, 0.64 mmol) in methanol (200 mL) was photolyzed for 9 h, under analogous conditions, and workup as in the earlier case gave 120 mg (66%) of **6**, mp 92 °C (mixture melting point).

In another run, a solution of **2** (0.2 g, 0.64 mmol) in acetone (150 mL) was photolyzed for 6 h under similar conditions; the solvent was removed under vacuum, and the residue was chromatographed over silica gel. Elution of the column with petroleum ether gave 128 mg (65%) of the phenanthro[9,10-*c*]furanone **15**,[3f] mp 259–260 °C (mixture melting point), after recrystallization from methanol. Further elution of the column with a mixture (1:4) of benzene and petroleum ether gave 30 mg (15%) of **13**,[3f] mp 124–125 °C (mixture melting point), after recrystallization from methanol.

Irradiation of 3,4,5-Triphenyl-2(5*H*)-furanone (13). A solution of **13** (0.2 g, 0.64 mmol) in benzene (140 mL) was saturated with oxygen and irradiated under an RPR (3500 Å) light source for 5 h. The solvent was removed under vacuum to give 162 mg (82%) of **15**, mp 259–260 °C (mixture melting point), after recrystallization from methanol.

Photolysis of 3-Methyl-3,4,5-triphenyl-2(3*H*)-furanone (3). A solution of **3** (0.1 g, 0.31 mmol) in benzene (100 mL) was irradiated under an RPR (3500 Å) light source for 2.5 h. Removal of the solvent gave a residue, which was chromatographed over silica gel. Elution with petroleum ether gave 12 mg (11%) of **11**, mp 210 °C, after recrystallization from methanol: IR ν_{max} (KBr) 3080, 3060, 2980 (CH), 1780 (C=O), 1600 (C=C) cm^{-1}; UV λ_{max} (ethanol) 226 nm (ϵ 1850), 256 (4500), 274 (1800, sh), 300 (1150) and 310 (1200); ^{1}H NMR (CDCl$_3$) δ 2.2 (3 H, s, CH$_3$), 7.8 (11 H, m, Ar), 8.75 (2 H, m, phenanthrene H^4

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and H^5 protons); mass spectrum, *m/e* (relative intensity) 324 (M^+, 100), 309 ($M^+ - CH_3$, 25), 296 ($M^+ - CO$, 99), 279 ($M^+ - CO_2H$, 39), and other peaks.

Anal. Calcd for $C_{23}H_{26}O_2$: C, 85.18; H, 4.94. Found: C, 85.15; H, 5.25.

Further elution of the column with a mixture (1:4) of benzene and petroleum ether gave 69 mg (69%) of the unchanged starting material (**3**), mp 118–119 °C (mixture melting point), after recrystallization from methanol. In several repeat runs, the photolysis of **3** was carried out under different conditins and solvents and the yields of products in each case are indicated in parentheses: benzene, oxygen saturated, 2.5 h (RPR, 3500 Å) (**11**, 55%; **3**, 15%); methanol, degassed, 2.5 h (RPR, 3500 Å) (**11**, 19%; **3**, 55%); methanol, oxygen saturated, 2.5 h (RPR, 3500 Å) (**11**, 58%; **3**, 16%); acetone, degassed, 2.5 h (RPR, 2537 Å) (**3**, 94%).

Photolysis of 3-Benzyl-3,4,5-triphenyl-2-(3*H*)-furanone (4). A solution of **4** (1.6 g, 4 mmol) in benzene (1.4 L) was photolyzed for 25 h under an RPR (3500 Å) light source in 10 lots. The combined photolysates were concentrated under vacuum and the residue was recrystallized from methanol to give 1.1 g (70%) of **12**, mp 225–226 °C: IR ν_{max} (KBr) 3060, 3030, 2930 (CH), 1795 (C=O, β,γ-unsaturated lactone), 1610 and 1600 (C=C) cm^{-1}; UV λ_{max} (methanol) 214 nm (ϵ 1950), 254 (2070), 273 (800, sh), 298 (500), 310 (500), 338 (80) and 356 (100); ^1H NMR ($CDCl_3$) δ 4.1 (2 H, q, J = 14 Hz; CH_2, inequivalent due to restricted rotation), 7.34 (16 H, m, Ar), 8.7 (2 H, m, phenanthrene H^4 and H^5 protons); mass spectrum, *m/e* (relative intensity) 400 (M^+, 17), 309 ($M^+ - CH_2CH_6H_5$, 100), 281 ($M^+ - CH_2C_6H_5, - CO$, 27), and other peaks.

Anal. Calcd for $C_{29}H_{20}O_2$: C, 87.00; H, 5.00. Found: C, 86.74; H, 4.60.

In several repeat experiments, **4** was irradiated in different solvents and conditions, and the yields of products under similar workup conditions are indicated in parentheses: benzene, oxygen saturated, 18 h (RPR, 3500 Å) (**12**, 90 mg); methanol, degassed, 23 h (RPR, 3500 Å) (**12**, 69%); methanol, oxygen saturated, 18 h (RPR, 3500 Å) (**12**, 87%); acetone, degassed, 18 h (RPR, 2537 Å) (**12**, 50%; **4**, 24% (recovery)).

Photolysis of 3,3′-Diphenyl-3,3′-bibenzo[*b*]furan-2,2′(3*H*,3′*H*)dione (16). A solution of **16** (0.2 g, 0.5 mmol) in cyclohexane (150 mL) was photolyzed under an RPR (2537 Å) light source for 8 h. Concentration of the solvent under vacuum gave a solid, which was filtered and subsequently recrystallized from a mixture (1:1) of methylene chloride and methanol to give 135 mg (67%) of the unchanged starting material (**16**), mp 175–176 °C (mixture melting point). The filtrate, after removal of the solid, was concentrated under vacuum and chromatographed over silica gel. Elution with a mixture (1:3) of benzene and petroleum ether gave 25 mg (12%) of the furanone **25**, mp 113–114 °C (mixture melting point), after recrystallization from methanol.

In another run, a solution of **16** (0.23 g, 0.55 mmol) in methanol (140 mL) was irradiated for 4 h, under analogous conditions. The photolysis was repeated again to photolyze, in all, 0.46 g (1.1 mmol) of **16**. The combined photolysates were concentrated under vacuum and the residue was chromatographed over silica gel. Elution of the column with a mixture (1:4) of benzene and petroleum ether gave 10 mg (2%) of the unchanged starting material (**16**), mp 175–176 °C (mixture melting point), after crystallization from a mixture (1:1) of methylene chloride and methanol. Further elution with a mixture (4:1) of benzene and petroleum ether gave 40 mg (10%) of the ester **34**,[17] mp 127–128 °C (mixture melting point), after recrystallization from methanol. Further elution of the column with benzene gave 200 mg (40%) of **31**,[13] mp 102–103 °C, after recrystallization from hexane: IR ν_{max} (KBr) 3560, 3480 (OH, intramolecular hydrogen bonded), 3060, 3020 and 2980 (CH), 1810 (C=O), 1620 (C=C); UV λ_{max} (methanol) 266 nm (ϵ 1230), 271 (1360).

Anal. Calcd for $C_{14}H_{10}O_3$: C, 74.33; H, 4.46. Found: C, 74.10; H, 4.40.

Irradiation of **16** in benzene under similar conditions resulted in the recovery of the unchanged starting material, **16** (90%), mp 175–176 °C (mixture melting point).

Photolysis of 5,5′-Dimethyl-3,3′-diphenyl-3,3′-bibenzo[*b*]furan-2,2′-(3*H*,3′*H*)-dione (17). A solution of **17** (1.5 g, 3.5 mmol, 1.5 mL) in methanol was photolyzed under an RPR (2537 Å) light source for 6 h. Removal of the solvent under vacuum gave a residue, which was chromatographed over silica gel. Elution with a mixture (1:4) of benzene and petroleum ether gave a small amount (85 mg, 6%) of the unchanged starting material (**17**), mp 158 °C (mixture melting point), after recrystallization from a mixture (1:1) of methylene chloride and methanol. Continued elution of the column with a mixture (4:1) of benzene and petroleum ether gave 150 mg (18%) of ester **35**,[13] mp 118–119 °C (mixture melting point), after recrystallization from methanol: IR ν_{max} (KBr) 3410 (OH), 3030, 2940 (CH), 1700 (C=O) cm^{-1}; UV λ_{max} (methanol) 285 nm (ϵ 1680); ^1H NMR ($CDCl_3$) δ 2.2 (3 H, s, CH_3), 3.75 (3 H, s, OCH_3), 5.1 (1 H, s, methine) and 7.0 (9 H, m, aromatic and OH); mass spectrum, *m/e* (relative intensity) 250 (M^+, 34), and other peaks.

Anal. Calcd for $C_{16}H_{16}O_3$: C, 75.00; H, 6.45. Found: C, 74.89; H, 6.66.

Further elution of the column with benzene gave 200 mg (25%) of **32**,[13] mp 105–106 °C (mixture melting point), after recrystallization from hexane: IR ν_{max} ($CHCl_3$) 3560, 3300 (OH, intermolecularly hydrogen bonded), 3020, 2920 (CH), 1800 (C=O), 1610 (C=C) cm^{-1}; UV λ_{max} (methanol) 268 nm (ϵ 1240), 274 (1400).

Anal. Calcd for $C_{15}H_{12}O_3$: C, 75.00; H, 5.00. Found: C, 74.79; H, 5.10.

Irradiation of **17** in benzene, under analogous conditions for 6 h resulted in the recovery of the unchanged starting material **17** (82%), mp 158 °C (mixture melting point).

Photolysis of 6,6′-Dimethyl-3,3′-diphenyl-3,3′-bibenzo[*b*]furan-2,2′-(3*H*,3′*H*)-dione (18). A solution of **18** (0.225 g, 0.5 mmol) in methanol (250 mL) was photolyzed under an RPR (2537 Å) light source for 4 h. Removal of the solvent under vacuum gave a residual solid, which was chromatographed over silica gel. Elution with petroleum ether gave a small amount (25 mg, 11%) of the unchanged starting material, mp 170–171 °C (mixture melting point), after recrystallization from a mixture (1:1) of methylene chloride and methanol. Continued elution of the column with a mixture (4:1) of benzene and petroleum ether gave 30 mg (11%) of the ester **36**,[13] mp 125–126 °C (mixture melting point), after recrystallization from methanol: IR ν_{max} (KBr) 3230 (OH), 3020, 2960 (CH), 1690 (C=O), 1600 (C=C) cm^{-1}; UV λ_{max} (methanol) 285 nm (ϵ 1650).

Anal. Calcd for $C_{16}H_{16}O_3$: C, 75.00; H, 6.45. Found: C, 74.88; H, 6.50.

Further elution of the column with benzene gave 90 mg (37%) of the furanone **33**, mp 124–125 °C (melting point), after recrystallization from hexane: IR ν_{max} ($CHCl_3$) 3550, 3320 (OH, intermolecularly hydrogen bonded), 3060, 3020, 2980 (CH), 1800 (C=O), 1610, 1600 (C=C) cm^{-1}; UV λ_{max} (methanol) 265 nm (ϵ 1300), 271 (1350).

Anal. Calcd for $C_{15}H_{12}O_3$: C, 75.00; H, 5.00. Found: C, 75.21; H, 4.88.

In a separate experiment, when **18** was irradiated for 6 h in benzene, under analogous conditions, the starting material (**18**) was recovered unchanged (78%), mp 170–171 °C (mixture melting point).

Thermolysis of 3,3,4,5-Tetraphenyl-2(3*H*)-furanone (1). A. In Diphenyl Ether. A solution of **1** (0.1 g, 0.25 mmol) in diphenyl ether (10 mL) was refluxed for 8 h, and the solvent was removed under vacuum. The residue was washed with petroleum ether and recrystallized from methanol to give 92 mg (92%) of the unchanged starting material (**1**), mp 138 °C (mixture melting point).

B. Neat Thermolysis. A sample of **1** (0.78 g, 2 mmol) was heated at ca. 350 °C for 5 h in a sealed tube. The reaction mixture was chromatographed on a silica gel column and eluted with a mixture (1:5) of benzene and petroleum ether to give 150 mg (20%) of the unchanged starting material (**1**), mp 138–139 °C (mixture melting point). Further elution of the column with a mixture (1:4) of benzene and petroleum ether gave 300 mg (42%) of the enone **5**, mp 152 °C (mixture melting point), after recrystallization from methanol.

In a repeat experiment, a sample of **1** (0.78 g, 2 mmol) was heated in a sealed tube for 0.25 h at ca. 450 °C, and the resultant mixture was recrystallized from methanol to give 580 mg (80%) of **5**, mp 152 °C (mixture melting point).

Thermolysis of 3,3,5-Triphenyl-2(3*H*)-furanone (2). A. In Diphenyl Ether. A sample of **2** (0.31 g, 1 mmol) in diphenyl ether (10 mL) was refluxed for 8 h. Removal of the solvent under vacuum gave a residual solid, which was washed with petroleum ether and later recrystallized from methanol to give 280 mg (90%) of the unchanged starting material (**2**), mp 120–121 °C (mixture melting point).

B. Neat Thermolysis. A sample of **2** (0.62 g, 2 mmol) was heated in a sealed tube at ca. 350 °C for 5 h and the reaction mixture was chromatographed over silica gel. Elution of the column with a mixture (1:9) of benzene and petroleum ether gave 0.13 g (21%) of the unchanged starting material (**2**), mp 120–121 °C (mixture melting point), after recrystallization from methanol. Subsequent elution of the column with a mixture (1:4) of benzene and petroleum ether gave 280 mg (55%) of the enone **6**, mp 92 °C (mixture melting point).

In a repeat experiment, a sample of **2** (0.62 g, 2 mmol) was heated in a sealed tube at ca. 450 °C for 0.25 h and the reaction mixture was recrystallized from methanol to give 450 mg (82%) of **6**, mp 92 °C (mixture melting point).

Thermolysis of 3-Methyl-3,4,5-triphenyl-2(3*H*)-furanone (3). A. In Diphenyl Ether. A sample of **3** (0.16 g, 0.5 mmol) in diphenyl ether (10 mL) was refluxed for 8 h and the solvent was removed under vacuum. The residual solid was washed with petroleum ether and then recrystallized from methanol to give 142 mg (88%) of the unchanged starting material (**3**), mp 118–119 °C (mixture melting point).

B. Neat Thermolysis. A sample of **3** (0.64 g, 2 mmol) was heated at ca. 310 °C for 5 h and the resultant mixture was chromatographed over silica gel. Elution with petroleum ether gave 300 mg (45%) of the unchanged starting material (**3**), mp 118–119 °C (mixture melting point). Subsequent elution with a mixture (1:4) of benzene and petroleum ether gave 200 mg (36%) of **37**,[18] mp 101 °C, (mixture melting point), after recrystallization from methanol. Further elution of the column with benzene gave a small amount (20 mg, 9%) of benzoic acid, mp 121 °C (mixture melting point).

Thermolysis of 3-Benzyl-3,4,5-triphenyl-2(3*H*)-furanone (4) in Diphenyl Ether. A solution of **4** (0.8 g, 2 mmol) in diphenyl ether (10 mL) was refluxed for 1 h, and the solvent was removed under vacuum to give a residual solid, which was washed with petroleum ether and later recrystallized from a mixture (1:1) of benzene and petroleum ether to give 755 mg (95%) of the furanone **38**, mp 154–155 °C: IR ν_{max} (KBr) 3060, 3020, 2920 (CH), 1750 (C=O), 1600 (C=C) cm^{-1}; UV λ_{max} (methanol) 215 nm (ϵ 3560), 278 (1100).

Anal. Calcd for $C_{29}H_{22}O_2$: C, 86.56; H, 5.47. Found: C, 86.68; H, 4.99.

Thermolysis of 3,3′-Diphenyl[3,3′-bibenzo[*b*]furan]-2,2′(3*H*,3′*H*)dione (16). A sample of **16** (0.46 g, 1.1 mmol) in diphenyl ether (10 mL) was refluxed for 1 h. Removal of the solvent under vacuum gave a residual solid, which was chromatographed over silica gel. Elution of the column with a mixture (1:3) of benzene and petroleum ether gave 200 mg (42%) of the furanone **25**,[13,33] mp 113–114 °C (mixture melting point), after recrystallization from methanol.

In a repeat experiment, a sample of **16** (1.0 g, 2.3 mmol) was refluxed in cumene (10 mL) for 0.5 h. Removal of the solvent and recrystallization from methanol gave 680 mg (68%) of **25**, mp 113–114 °C (mixture melting point).

Thermolysis of 5,5′-Dimethyl-3,3′-diphenyl[3,3′-bibenzo[*b*]furan]-2,2′(3*H*,3′*H*)-dione (17) in Cumene. A sample of **17** (1.1 g, 2.3 mmol) in cumene (15 mL) was refluxed for 1 h. Removal of the solvent and recrystallization from methanol gave 675 mg (65%) of the furanone **26**, mp 105–106 °C (mixture melting point).

Thermolysis of 6,6′-Dimethyl-3,3′-diphenyl[3,3′-bibenzo[*b*]furan]-2,2′(3*H*,3′*H*)-dione (18) in Cumene. A sample of **18** (0.85 g, 2 mmol) in cumene (15 mL) was refluxed for 1 h and the solvent was removed under reduced pressure. The residue, thus obtained, was recrystallized from methanol to give 530 mg (62%) of **27**, mp 122 °C (mixture melting point).

Laser Flash Photolysis. The laser flash photolysis experiments were carried out in a computer-controlled setup using a Tachisto excimer (248 nm, Kr, F_2) and a Molectron UV-400 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 available in previous publications[33,34] from the Radiation Laboratory.

Pulse Radiolysis. For spectrophotometric pulse radiolsis, 5-ns electron pulses from the Notre Dame 7-MeV ARCO LP-7 linear accelerator were used at a dose rate of $\sim 2 \times 10^{16}$ (eV/g)/pulse. A description of the setup is available elsewhere.[35] The signals were recorded by a Biomation 6500 transient recorder interfaced with an LSI-11 microcomputer system.

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Colloidal Catalyst-Coated Semiconductors in Surfactant Vesicles: In Situ Generation of Rh-Coated CdS Particles in Dihexadecylphosphate Vesicles and Their Utilization for Photosensitized Charge Separation and Hydrogen Generation

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Abstract: Colloidal ca. 40-Å diameter CdS semiconductor particles were in situ generated and in situ coated by rhodium in 800–1000-Å diameter single-bilayer dihexadecylphosphate (DHP) vesicles. The vesicles controlled the size and the stability of the CdS particles, generated by H_2S from adsorbed Cd^{2+} ions. CdS fluorescence could be observed only from particles formed at the inside surface of the vesicles and when the sonication pH was higher than 6. No fluorescence could be detected in CdS colloids generated from Cd^{2+} added to already formed vesicles. Quenching of CdS fluorescence by methylviologen (MV^{2+}), Rh^{3+}, and thiophenol (PhSH), externally added or cosonicated with DHP, was determined. Externally added MV^{2+} and Rh^{3+} did not quench CdS fluorescence, but externally added PhSH did. Photolysis by visible light, in the absence of oxygen, of DHP-vesicle-stabilized, rhodium-coated colloidal CdS in the presence of PhSH as electron donor led to hydrogen formation which could be sustained until complete consumption of PhSH. Effects of temperature and PhSH and catalyst concentrations on the hydrogen production were determined. Turnover numbers, limited by the maximum tolerable amount of PhSH in the vesicles, were 5.4 and 13.6 for CdS and Rh, respectively.

The current approach to artificial photosynthesis[1-4] involves the separate optimizations of the sacrificial reduction and oxidation half-cells. In the reduction half-cell, hydrogen is generated at the expense of a sacrificial electron donor, D. In homogeneous solution, excitation of the sensitizer, S, is followed by electron transfer

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