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Sensitized Photorearrangement of 3,3,5-Triaryl-2(3*H*)-furanones to 3,4,5-Triaryl-2(5*H*)-furanones. Steady-State and Laser Flash Photolysis Investigations[1]

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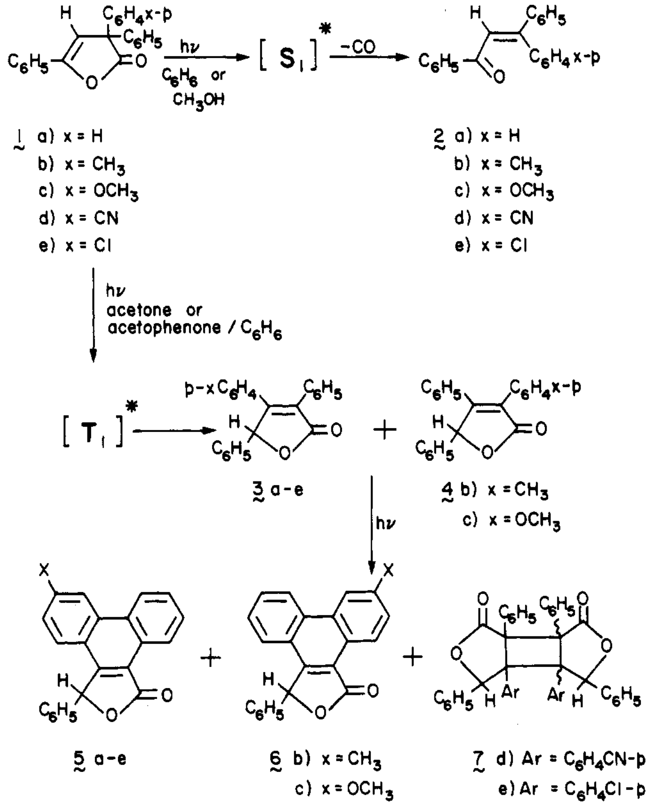
A novel photorearrangement of 3,3,5-triaryl-2(3*H*)-furanones **1a–e** under acetone or acetophenone sensitization is reported. Sensitized irradiation of **1a–e** in benzene gave a mixture of the photorearranged 2(5*H*)-furanones **3** and **4**, along with the corresponding phenanthrofuranones **5** and **6**, respectively. In contrast, the direct irradiation of **1a–e** gave the corresponding decarbonylated products **2a–e**. On the basis of product analysis, *p*-chlorophenyl, *p*-cyanophenyl, and *p*-tolyl groups were found to be better migrating groups than phenyl from the C-3 carbon, whereas the *p*-anisyl group was found to have a smaller migratory aptitude than phenyl. The preferential migration of *p*-cyanophenyl over phenyl and of phenyl over *p*-anisyl as well as the formation of the methanol adduct **14** in the acetophenone-sensitized irradiation of **1a** in methanol suggests the involvement of photointermediates with significant ionic character. The direct observation of the 2(3*H*)-furanone triplets by laser flash photolysis enabled us to estimate the aryl group migrating rates at $\leq 1.5 \times 10^6$ s^{-1}, except for the *p*-cyanophenyl group for which the rate is higher by 1 order of magnitude.

Introduction

Past investigations have shown that unsaturated lactones undergo a variety of phototransformations, some of which include decarbonylation,[3-6] decarboxylation,[7] solvent addition to double bonds,[8-10] migration of aryl substituents,[10] and dimerization.[11] In a recent publication,[12] we have reported the phototransformations of a number of 2(3*H*)-furanones and bis(benzofuranones), based on steady-state irradiation, product analysis, and laser flash photolysis. The two prominent pathways for the photoreactions of 2(3*H*)-furanones include a singlet-mediated decarbonylation to give α,β-unsaturated carbonyl compounds and cyclization leading to 4a,4b–dihydrophenanthrenes. The bis(benzofuranones), on the other hand, give products, explainable in terms of facile homolytic fission of these substrates to give a pair of benzofuranoxy radicals, which subsequently undergo further transformation. Also, in our earlier paper[12] we had briefly reported on our preliminary findings of an interesting photorearrangement of 3,3,5-triphenyl-2(3*H*)-furanone (**1a**) to 3,4,5-triphenyl-2(5*H*)-furanone (**3a**) under acetone sensitization.

Scheme I



In the present study, we have examined in detail the sensitized photorearrangements of several 3,3,5-triaryl-2-(3*H*)-furanones and the migratory aptitudes of different substituted aryl groups present at the C-3 position of these furanones. In some respects, the substituent effect on the relative rates of photochemical aryl group migration is found to be different from that in 2(5*H*)-furanones and cyclohexenones.[13] The laser flash photolysis observation of 2(3*H*)-furanone triplets enabled us to conclude that the migration of aryl groups occurs on a microsecond time scale (except for *p*-cyanophenyl group which migrates at ~10 times faster rate). The 2(3*H*)-furanones we have examined include 3,3,5-triphenyl-2(3*H*)-furanone (**1a**), 3,5-diphenyl-3-(4-methylphenyl)-2(3*H*)-furanone (**1b**), 3,5-diphenyl-3-(4-methoxyphenyl)-2(3*H*)-furanone (**1c**), 3-(4-cyanophenyl)-3,5-diphenyl-2(3H)-furanone (**1d**), and 3-

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[1] Document No. NDRL-2881 from the Notre Dame Radiation Laboratory.

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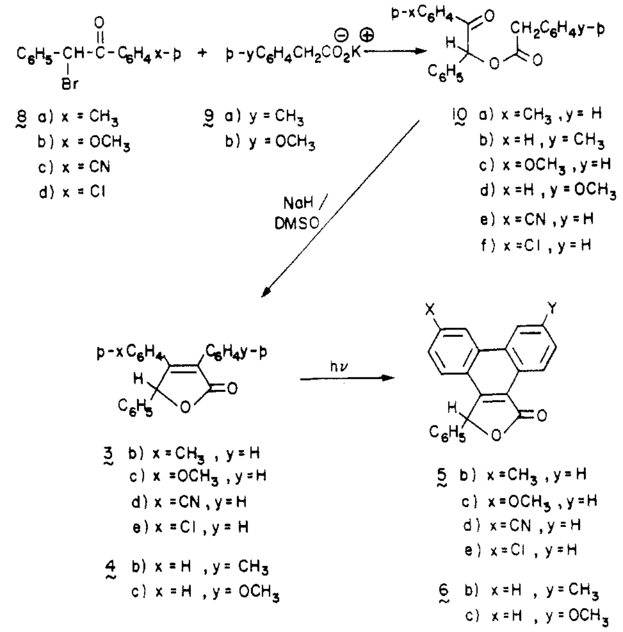
Scheme II



(4-chlorophenyl)-3,5-diphenyl-2(3*H*)-furanone (**1e**).

Results

1. Preparative Photochemistry and Product Identification. Direct irradiation of a solution of the 2-(3*H*)-furanone **1a** in benzene or methanol gave the decarbonylated product 1,3,3-triphenylprop-2-en-1-one (**2a**)[14] in 87% and 66% yields, respectively. In contrast, when the irradiation was carried out in acetone, two products resulting from phenyl group migration from the C-3 to C-4 position, viz. 3,4,5-triphenyl-2(5*H*)-furanone (**3a**, 15%)[10] and 3-phenylphenanthro[9,10-*c*]furan-1(3*H*)-one (**5a**, 65%),[10] were obtained (Scheme I). Similar results were obtained when the irradiation of **1a** was carried out in benzene, using acetophenone as sensitizer, under conditions wherein the sensitizer absorbed all the light. On the other hand, when the sensitized irradiation was carried out in methanol, the product obtained was *cis*-5-methoxy-4,5-dihydro-3,4,5-triphenyl-2(3*H*)-furanone (**14**) in 75% yield (Scheme III).

To gain insight into the electronic makeup of the excited state in the photorearrangements of 2(3*H*)-furanones, we have examined the reactions of different furanones **1b**-**e**, containing both electron-withdrawing and -donating substituents in the para position of one of the C-3 phenyl groups. Thus, the irradiation of **1b** in benzene or methanol gave 1,3-diphenyl-3-(4-methylphenyl)prop-2-en-1-one (**2b**), the decarbonylated product in 84% and 60% yields, respectively, whereas irradiation in benzene, under acetophenone sensitization, gave a mixture of the rearranged 2(5*H*)-furanones **3b** and **4b** (30%) in a 3:2 ratio, along with the corresponding phenanthrofuranones **5b** and **6b** (46%) in the same ratio (Scheme I). The structures of all the products were established on the basis of spectral data and also by comparison with authentic samples prepared through the route outlined in Scheme II.[10,15]

Similarly, acetophenone-sensitized irradiation of **1c** gave a mixture of the 2(5*H*)-furanones **3c** and **4c** (29%) in a 2:3 ratio, along with the corresponding phenanthrofuranes **5c** and **6c** (49%), also in the same ratio. Direct irradiation of **1c** in benzene or methanol gave the decarbonylated product **2c** in a 64% yield, in each case.

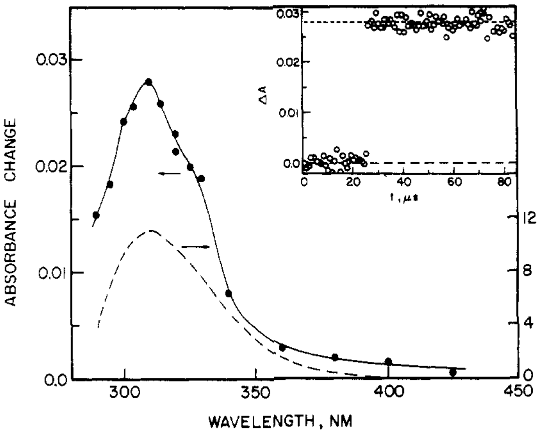


Figure 1. Absorbance changes at 3 μs following 248-nm laser flash photolysis of furanone **1d** in methanol. The broken curve is the difference absorption spectrum of **2d** and **1d** in methanol. The inset shows a kinetic trace at 310 nm resulting from 248-nm laser flash photolysis of **1d**.

Likewise, the direct irradiation of **1d** in benzene and methanol gave the decarbonylated product **2d** in 85% and 87% yields, respectively. However, when the irradiation of **1d** was carried out under acetophenone sensitization, only one of the two possible rearranged 2(5*H*)-furanones, namely, 4-(4-cyanophenyl)-3,5-diphenyl-2(5*H*)-furanone (**3d**,[10] 16%) was obtained, along with the corresponding phenanthrofuranone **5d** (18%) and a [2 + 2] photodimer, tentatively assigned as **7d** (40%) (Scheme I).

The photolysis of **1e** in benzene or methanol gave the decaronylated product **2e** in 82% and 76% yields, respectively, whereas under acetophenone sensitization, a mixture of 4-(4-chlorophenyl)-3,5-diphenyl-2(5*H*)-furanone (**3e**, 13%), the phenanthrofuranone **5e** (13%), and the [2 + 2] photodimer **7e** (53%) was obtained. It may be pointed out here that under acetophenone-sensitized irradiation of **1d** and **1e**, the photodimers were formed in greater amounts when the starting concentrations of the 2(3*H*)-furanones were higher (~10^{-2} M or more), whereas from dilute solutions (~10^{-3} M) the photoearranged products were obtained in appreciable yields.

1e was also subjected to photolysis under acetophenone sensitization in benzene for varying lengths of time. At low conversion, namely, 34% loss of starting material, the photoproduct **5e** is not observed. As expected, with increasing irradiation time, the amount of **5e** and **7e** in the photolysate progressively increases while that of **3e** goes through a maximum. Under any condition, the isomer 3-(4-chlorophenyl)-4,5-diphenyl-2(5*H*)-furanone is not formed in detectable amounts.

2. Laser Flash Photolysis Studies. In order to shed light on the precursors and intermediates that lead to the photoproducts observed in the course of steady-state photolysis (vide supra), 2(3*H*)-furanones **1a**-**d** and 2-(5*H*)-furanones **3a**,**b**,**d** and **4b**,**c** were subjected to laser flash photolysis studies. Attempts were made to observe transients in terms of their absorption at 250-750 nm over 100 ns-100 μs following nanosecond laser pulse excitation. Both direct excitation and triplet sensitization were employed to photogenerate the intermediates.

(a) Direct Excitation of 2(3*H*)- and 2(5*H*)-Furanones. Upon 248-nm laser excitation, methanolic solutions of 2(3*H*)-furanones **1a**-**e** give rise to photoproducts characterized by absorption maxima (λ_{max}^{P}) at 300-335 nm and showing no sign of decay over the longest time scale (~100 μs) used in our experiments. A repre-

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Table I. Photoproduct Absorption Maxima and Yields in Methanol (λ_{ex} = 248 nm)[a] at 295 K

substr	λ_{max}^{P}, nm[b]	ϕ_P
1a	300	0.32
1b	330	0.27
1c	330	0.20
1d	300	0.22
1e	310	0.30
3a	325, 490	0.61 (0.42)[c]
3b	330, 490	0.53 (0.36)[c]
3d	335, 500	0.45 (0.34)[c]
4b	325, 490	0.61 (0.34)[c]
4c	330, 490	0.69 (0.38)[c]

[a] Except for the parenthesized ϕ_P data in benzene obtained with λ_{ex} = 308 nm. [b] ±5 nm. [c] Calculated with the assumption that ϵ_{max}^{P} of each of 4a,4b-dihydrophenanthrenes at 490–500 nm is 6.8 × 10^3 M^{-1} cm^{-1} (see text).

sentative case with **1e** as the substrate is illustrated in Figure 1. Oxygen (2.1 mM) does not affect the yields or decay behaviors of the "permanent" photoproducts. The photoproduct absorption maxima (λ_{max}^{P}), listed in Table I, show a substituent effect similar to that of the ground-state absorption maxima of the photodecarbonylation products **2a–e**. For example, λ_{max}^{P}'s (330–335 nm) are found to be most red-shifted in the case of **1b** and **1c**; the decarbonylation products **2b,c** obtained from these two substrates have λ_{max} at 334–336 nm, compared to 296–312 nm for **2a,d,e** (in methanol). On the basis of spectral similarity with **2a–d**, permanent nature, and insensitivity toward oxygen, we assign the photoproducts observed under direct laser excitation of **1a–e** as the α,β-unsaturated ketones **2a–e**. In our time-resolved measurements, the two-bond cleavage leading to photoextrusion of CO appears as a concerted process occurring within nanoseconds of laser photoexcitation (that is, we do not observe the biradicals that could be formed from the cleavage of one of the bonds to the carbonyl group).

The 308- or 248-nm laser flash photolysis of 2(5*H*)-furanones **3a,b,d** and **4b,c** in benzene or methanol results in the formation of long-lived photoproducts displaying dual absorption maxima at 325–335 and 490–500 nm. The photoproduct absorption spectrum with **3b** as the substrate in methanol is shown in Figure 2. The long-lived nature of the photoproducts is suggested by the fact that they undergo little or no decay (≤5%) on the longest time scale (~100 μs). In view of the fact that phenanthrene derivatives **5a–e** and **6b,c** are isolated in high yields in the course of exhaustive photolysis of **1a–e** under triplet sensitization as well as of direct photolysis of **3b–e** and **4b–c** (vide supra), it seems plausible that the observed 330/490-nm species are 4a,4b-dihydrophenanthrenes, i.e., products of cyclization involving the vicinal phenyl groups in cis configuration at the 3- and 4-positions of the 2-(5*H*)-furanones. This assignment is supported by the similarity of the absorption spectra with those of 4a,4b-dihydrophenanthrenes produced from *cis*-stilbene and diphenylcyclopentene under steady-state photolysis at subambient temperatures.[16] Also, in an earlier study, we have observed spectrally and kinetically similar photoproducts resulting from the laser flash photolysis of 4,5-diaryl-substituted 2(3*H*)-furanones.[12]

Estimates were made for photoproduct yields (ϕ_P) from 2(3*H*)- and 2(5*H*)-furanones under direct laser excitation. For actinometry for solutions in methanol (λ_{ex} = 248 nm) and in benzene (λ_{ex} = 308 nm), use was made of the triplet formation of naphthalene (in cyclohexane, λ_{max}^{T} = 414 nm, ϵ_{max}^{T} = 24.5 × 10^3 M^{-1} cm^{-1}, and ϕ_T = 0.75)[17] and benzophenone (in benzene, λ_{max}^{T} = 532 nm, ϵ_{max}^{T} = 7.6 × 10^3 M^{-1} cm^{-1}, and ϕ_T = 1.0),[17] respectively. To calculate ϕ_P, we used eq 1 where ΔA's represent end-of-pulse absorbance

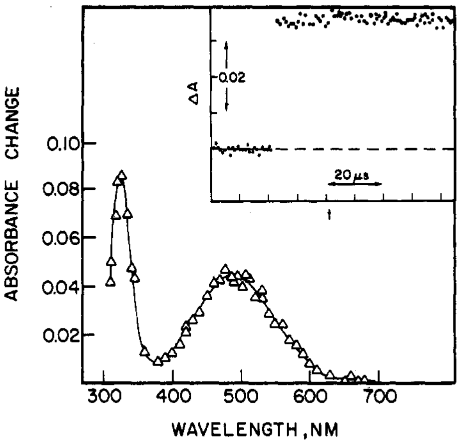

Figure 2. Transient absorption spectra at 3.5 μs following 248-nm laser flash photolysis of **4b** in methanol. Inset: a typical kinetic trace for this system at 495 nm.

$$\phi_P = \phi_T \frac{\Delta A_P}{\Delta A_T^{R}} \frac{\epsilon_T^{R}}{\epsilon_P} \qquad (1)$$

changes, ϵ's are extinction coefficients at the monitoring wavelengths, and R and P designate reference (naphthalene or benzophenone) and photoproduct, respectively. For decarbonylation products (i.e., α,β-unsaturated ketones **2a–e**), ϵ_P's were measured from the isolated compounds. For dihydrophenanthrenes, ϵ_P's at 490–500 nm were assumed to be the same as that reported for 4a,4b-dihydrophenanthrene from *cis*-stilbene (6.8 × 10^3 M^{-1} cm^{-1})[16] in 2:1 methylcyclohexane and isohexane at 263 K. The ϵ_P data are given in Table I. In spite of large uncertainties in ϵ_P's and hence ϕ_P's (Table I), both photodecarbonylation and photocyclization can be considered as efficient photoreactions of 2(3*H*)- and 2(5*H*)-furanones, respectively.

(b) Triplet Sensitization. The photoreaction of major interest in this work is the triplet-sensitized rearrangement of 2(3*H*)-furanones to 2(5*H*)-furanones.. Hence, the properties of the triplets of 2(3*H*)-furanones **1a–d** are mechanistically relevant. The 2(3*H*)-furanones under study do not absorb significantly at ≥320 nm. Thus, they could be examined as acceptors of energy from benzophenone and acetophenone triplets produced by laser excitation of the ketones at 337 or 355 nm. Note that the 2(3*H*)-furanones under consideration contain styrene moieties constrained into planar geometries. Since their triplet energies should not be very different from the spectroscopic triplet energy of styrene (E_T = 62 kcal mol^{-1}),[18] these substrates should quench the aromatic ketone triplets via exothermic energy transfer.

Upon 337- or 355-nm laser excitation of benzophenone (0.04–0.06 M) or acetophenone (~0.1 M) in the presence of 5–25 mM **1a–d** in benzene, we observe short-lived transients with absorption maxima at 335–340 nm. Two representative spectra are shown in Figure 3. The transients decay by clean first-order kinetics leading to weak residual absorptions with maxima <320 nm (see kinetic traces in Figure 3). On the basis of their quenching behaviors toward oxygen, 2,5-dimethyl-2,4-hexadiene, and

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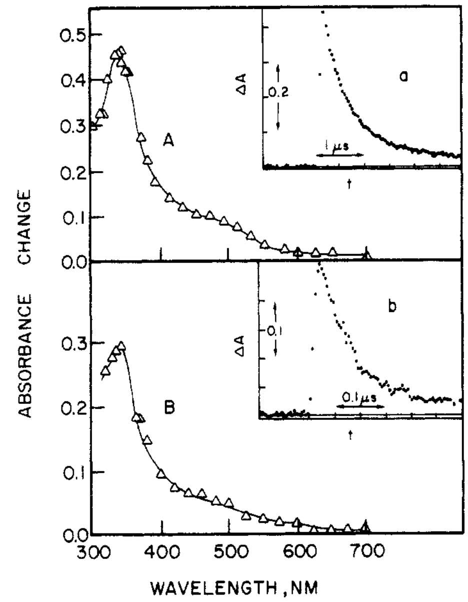


Figure 3. Transient absorption spectra (A) at 0.5 μs following 355-nm laser excitation of benzophenone (0.02 M) in the presence of 30 mM **1b** and (B) at 0.04 μs following 355-nm laser excitation of acetophenone (0.05 M) in the presence of 30 mM **1d**. Solvent: benzene. Insets: kinetic traces showing the triplet decay at 340 nm for the two furanones.

Table II. Spectral and Kinetic Properties of 2(3*H*)-Furanone Triplets in Benzene at 295 K

substr	$\lambda_{max}{}^T$, nm[a]	τ_T, μs[b,c]	$10^{-9}k_{q,O_2}{}^T$,[b] M^{-1} s^{-1}
1a	335	0.92 (1.03)	1.6 (2.1)
1b	335	0.75 (0.99)	1.8 (2.0)
1c	340	0.86 (1.02)	1.5 (1.9)
1d	335	0.061 (0.036)	1.6
1e	340	0.68 (0.70)	1.7 (1.8)

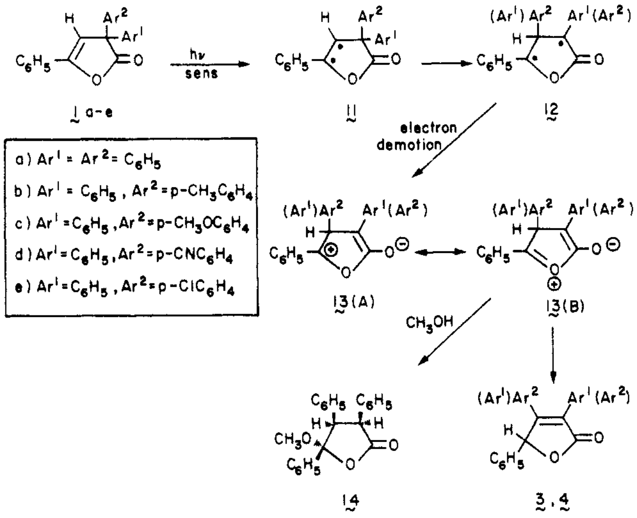
[a] ±5 nm. [b] ±15%; the data in the parentheses are in methanol. [c] Triplet lifetimes in benzene were obtained from extrapolation to zero substrate concentrations; those in methanol were measured at ~10 mM substrate concentrations.

ferrocene, we assign the 335–340-nm transients as the triplets of the 2(3*H*)-furanones. The rate constants for the quenching of the triplet of **1a** by the aforementioned quenchers in benzene are 1.6 × 10^9, 9.8 × 10^8, and 5.0 × 10^9 M^{-1} s^{-1}, respectively.

The triplet decay lifetimes were measured in benzene as functions of ground-state concentrations in the range 4–25 mM. The self-quenching rate constants were negligible ($\leq 10^7$ M^{-1} s^{-1}). The triplet lifetimes (τ_T) in benzene obtained by extrapolation to zero concentrations are all in the submicrosecond time domain (Table II). In Table II are also given the triplet lifetimes in methanol measured under sensitization by *p*-methoxyacetophenone at ca. 10 mM substrate concentrations. Note that except for **1d**, τ_T's in methanol are slightly longer than those in benzene. The oxygen-quenching rate constants ($k_{q,O_2}{}^T$, Table II) are all in the vicinity of $^1/_9\ k_{diff}$, suggesting energy transfer to be important in the interaction of the styrene-like, but planar, triplets with oxygen.

The triplets of the 2(5*H*)-furanones also were generated in benzene under energy-transfer sensitization by benzophenone triplet (λ_{ex} = 355 nm). These are characterized by broad and featureless absorption spectra with maxima at 360–380 nm (except for **4c**, where $\lambda_{max}{}^T$ is red-shifted to 440 nm). The triplet lifetimes measured at 1 mM substrate concentrations are in the range 4–10 μs. These transients are not produced at all under direct photolysis of the 2(5*H*)-furanones. Also, no long-lived residual absorptions at 490–500 nm, attributable to 4a,4b-dihydrophenanthrenes, are observed following the decay of the 2(5*H*)-furanone triplets. These results establish that the photocyclization reaction leading to dihydrophenanthrenes is singlet-mediated and that its occurrence in the course of the sensitized photolysis of 2(3*H*)-furanones is due to direct light absorption by 2(5*H*)-furanones (initial photoproducts) at a later stage of the photolysis. As expected, the triplet lifetimes (4–10 μs) of the 3,4,5-triaryl-2(5*H*)-furanones under consideration are significantly longer than those (<1 ns) estimated for photoreactive 3,5,5-triaryl-2-(5*H*)-furanones studies by Padwa and co-workers.[10] The latter 2(5*H*)-furanones undergo C-5 to C-4 aryl group migration in the triplet state, the lifetime of which has been measured by piperylene quenching of the photoreaction under steady-state condition.[10]

Scheme III

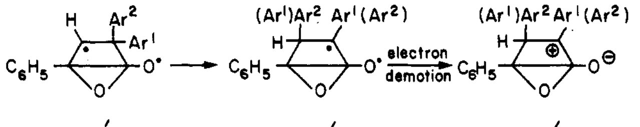


Discussion

The photochemical rearrangement of the 2(3*H*)-furanones **1a–e** to give the corresponding 2(5*H*)-furanones and the subsequent formation of the phenanthrofuranones **5** and **6** can be explained in terms of the pathway shown in Scheme III, involving the triplet excited state. In the triplet excited state, which can also be visualized in terms of a diradical structure (**11**), one of the C-3 aryl groups migrates through a bridged transition state to give the rearranged diradical intermediate **12**. Electron demotion in **12** will lead to a zwitterionic intermediate described by structures **13(A)** and **13(B)**. In the presence of methanol, for example, the zwitterionic intermediate is trapped to give the methanol adduct **14**. In the absence of any hydroxylic solvents, the zwitterionic intermediate undergoes a hydride shift to give the rearranged 2(5*H*)-furanones **3** and **4**. These furanones, in turn, absorb light and undergo further photocyclization leading to dihydrophenanthrofuranones; the latter give the phenanthrofuranones **5** and **6** through air-oxidation (under the conditions of workup). Alternatively, these 2(5*H*)-furanones can undergo [2 + 2] photocycloaddition, leading to the dimeric products **7**.

The observed migratory aptitudes of the para-substituted phenyl groups at C-3 position are in support of the pathway outlined in Scheme III. In the case of 5,5-diaryl-2(5*H*)-furanones in benzene, Padwa et al.[10] have observed that *p*-anisyl or *p*-cyanophenyl groups migrate in preference to a phenyl group. This has been attributed to the lower free energy of the bridged transition state in which the free valence is stabilized by the para substituent of the migrating aryl group. For the substrates under study, we have observed complete migration of *p*-chlorophenyl and *p*-cyanophenyl groups (against phenyl) and a preference of phenyl group migration over *p*-anisyl group. This latter trend was also observed by Padwa et al.[10] in the case of 2(5*H*)-furanones, when the irradiations were carried out in alcoholic solvents. This has been attributed to the stabilization of the positive charge developed at the C-5 center of the furanones by the substituents on the nonmigrating aryl group. Our results with 2(3*H*)-furanones in benzene are compatible with the view that the rearrangement proceeds directly from the triplet state and not from any subsequent ground-state zwitterionic intermediates. The preferential migration of *p*-chlorophenyl and *p*-cyanophenyl groups over phenyl group migration in the 2(3*H*)-furanones under investigation suggests that the C-4 center (migration termini) in the excited state of these furanones has odd-electron character. The high preference of *p*-cyanophenyl group migration agrees well with that observed in analogous triplet-mediated photorearrangements of cyclohexenones,[13] naphthalenones,[19] and 2-(5*H*)-furanones.[10]

The relative reluctance of the *p*-anisyl group to migrate is difficult to explain in terms of the diradical structures shown in Scheme III. It suggests that in the course of aryl group migration the electron density at C-3 is decreased and that the positive center at this position is stabilized by the *p*-anisyl group. Although formally nonconjugated, the styryl and carbonyl groups in 2(3*H*)-furanones are expected to interact strongly through favorable π orbital overlap. That the latter does occur is evident from the fact that the diene quenching of the 2(3*H*)-furanone triplets is far less than diffusion-controlled ($k_q^T \leq 10^9$ M^{-1} s^{-1}), suggesting a considerable lowering of E_T (relative to that of styrene, $E_T = 62$ kcal mol^{-1}). In light of the interaction of styrene/carbonyl groups, one can invoke valence-bond structures (shown below) that would give an ionic character to the product of aryl group migration with positive charge located at C-3. It is proposed that the biradicaloid product, **12′**, of aryl group migration has a significant ionic character and this ionic character is augmented by the *p*-anisyl group at the 3-position.



11′ 12′ 13′

The short lifetimes of 2(3*H*)-furanones **1a–d** are indicative of their photoreactive nature. These lifetimes (Table II) are intermediate between those of the triplets of styrenes (20–90 ns in methanol), which are recognized to exist in orthogonal configurations,[20] and those of the triplets of 3,4,5-triaryl-substituted 2(3*H*)-furanones[12] (8–12 μs), which cannot undergo the sensitized rearrangement. Note that furanone **1d** has τ_T significantly shorter than τ_T's of its analogues (Table II). This probably reflects a higher propensity of the *p*-cyanophenyl group to migrate, rather than an enhanced intersystem crossing ($T_1 \rightsquigarrow S_0$) in this system. If the latter were true, the sensitized photoreactivity of **1d** would be relatively sluggish. Steady-state photolysis studies show the opposite to be true.

The triplet lifetime data allow us to make direct estimates of the rates of intramolecular aryl group migration in the triplets of 3,3,5-triaryl-2(3*H*)-furanones. Since the observed τ_T's (Table II) are more than 10 times shorter than those of related 2(3*H*)-furanones in which the sensitized photorearrangement cannot occur,[12] it is reasonable to assume that the triplet decay of the photoreactive 2-(3*H*)-furanones (**1a–d**) is predominantly controlled by the aryl group migration (that is, the quantum yield, ϕ_{PR}, of the photorearrangement is close to unity). This should be particularly true in the case of **1d** where τ_T is unusually short (Table II). On the basis of $\phi_{PR} \leq 1$, the upper limits of the rate constants for triplet-state migration of the phenyl group in **1a** and of the *p*-cyanophenyl group in **1d** are calculated to be 5.4×10^5 and 1.6×10^7 s^{-1}, respectively (in benzene). These rates are substantially smaller than the migrating rates of the same aryl groups (1.8×10^9 and 9×10^9 s^{-1} in benzene) in 3,5,5-triaryl-2(5*H*)-furanone triplets, estimated by piperylene quenching studies.[10] Also, note that τ_T of **1c** is nearly the same as that of **1a** (Table II), suggesting that the *p*-anisyl group as a migrant is far inferior to the *p*-cyanophenyl group and that is capability to help migrate the geminal phenyl group is only mediocre.

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 Beckman DB, Cary 17, or Cary 219 spectrophotometers. The NMR traces were recorded on Varian A-60 or EM-390 or Brucker WP-80 spectrometers, using tetramethylsilane as internal standard. The mass spectra were recorded on a Hitachi RMU-6E single focussing mass spectrometer or a Varian Mat CH 7 mass spectrometer at 70 eV. Irradiations were carried out in Srinivasan-Griffin-Rayonet photochemical reactor (RPR 2537, 3000 or 3500 Å) or using a Hanovia 450-W medium pressure mercury lamp in a quartz jacketted immersion well.

Starting Materials. The furanones **1a**,[14] mp 120–121 C, **1b**,[21] mp 109–110 °C, **1c**,[21] mp 92–93 °C, and **1d**[21] mp 114–115 °C, were prepared by reported procedures. Solvents for steady-state photolysis experiments were purified and distilled before use. Aldrich Gold-Label solvents were used for laser studies. Petroleum ether used was the fraction with bp 60–80 °C.

Preparation of 3-(4-Chlorophenyl)-3,5-diphenyl-2(3*H*)-furanone (1e). To a mixture of *p*-chlorobenzil[22] (4.89 g, 20 mmol) and acetophenone (2.4 g, 20 mmol) in ethanol (25 mL) was added an ethanol solution of potassium hydroxide (2 g in 5 mL). The mixture was stirred at room temperature (~30 °C) for 2 h and kept in a refrigerator for 2 days. The solid material that separated out was collected and washed with ethanol to give a mixture (4.0 g, 69%, mp 82–85 °C) of 2-(4-chlorophenyl)-1,4-diphenylbut-2-ene-1,4-dione and 1-(4-chlorophenyl)-2,4-diphenylbut-2-ene-1,4-dione: IR ν_{max} (KBr) 1665 and 1645 (C=O) cm^{-1}. This mixture of the 1,4-diones (1.73 g, 5 mmol) was heated at 270 °C for 5 h. The residue was extracted with methylene chloride and chromatographed over silica gel. Elution with a mixture (1:9) of benzene and petroleum ether gave **1e** (1.0 g, 57%), mp 98–99 °C: IR ν_{max} (KBr) 3080, 3060, 3030 (CH), 1795 (C=O), 1650, 1600 (C=C) cm^{-1}; UV λ_{max} (methanol) 218 nm (ϵ 31 400), 230 (22 430), 270 (18 600), 294 (5770 sh); ^{1}H NMR (CDCl$_3$) δ 6.36 (1 H, s, vinylic), 7.66 (14 H, m, Ar).

Anal. Calcd for $C_{22}H_{15}O_2Cl$: C, 76.30; H, 3.78. Found: C, 76.56; H, 3.64.

Photolysis of 3,3,5-Triphenyl-2(3*H*)-furanone (1a). A solution of **1a** (300 mg, 1 mmol) in benzene (250 mL) was irradiated for 9 h (RPR, 2537 Å). Removal of the solvent and recrystallization of the residue from methanol gave 240 mg (87%) of **2a**,[14] mp 92 °C (mixture melting point). Irradiation of **1a** (200 mg, 0.64 mmol) in methanol (200 mL) for 9 h and workup as in

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the earlier case gave 120 mg (60%) of **2a**, mp 92 °C (mixture melting point).

In a repeat run, a solution of **1a** (200 mg, 0.64 mmol) in acetone (150 mL) was photolyzed for 6 h, under analogous conditions. The residual solid, on removal of the solvent, was chromatographed over silica gel. Elution with petroleum ether gave 128 mg (65%) of the phenanthro[9,10-*c*]furanone **5a**,[10] 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 **3a**,[10] mp 124–125 °C (mixture melting point), after recrystallization from methanol. In another experiment, a solution of **1a** (100 mg, 0.32 mmol) in benzene (200 mL), containing acetophenone (60 mg, 0.5 mmol) was irradiated for 3 h (RPR, 3500 Å) by using a 2 mM solution of naphthalene in benzene as filter. Workup as in the earlier case gave 50 mg (51%) of **5a**, mp 259–260 °C (mixture melting ont), and 20 mg (20%) of **3a**, mp 124–125 °C (mixture melting point).

In another run, a solution of **1a** (300 mg, 1 mmol) in methanol (200 mL) was irradiated for 3 h (RPR, 3500 Å) in the presence of acetophenone (120 mg, 1 mmol). Removal of the solvent under vacuum gave 250 mg (75%) of **14**, mp 146–147 °C (lit.[10] mp 142–143 °C), after recrystallization from a mixture (1:1) of benzene and petroleum ether: IR ν_{max} (KBr) 3060, 3020, 2990, 2975, and 2940 (CH), 1770 (C=O), 1600 (C=C) cm^{-1}; UV λ_{max} (methanol) 248 nm (ϵ 9930), 258 (8040, sh), 312 (1000); ^{1}H NMR (CDCl$_3$) δ 3.26 (3 H, s, methoxy), 4.26 (1 H, d, J = 8.0 Hz, methine), 5.1 (1 H, d, J = 8.0 Hz, methine), and 7.08 (15 H, m, Ar); ^{13}C NMR (CDCl$_3$) δ 50.71, 51.49, 59,84, 110.22, 126.78, 126.86, 127.71, 127.89, 127.99, 128.49, 129.14, 129.29, 133.00, 134.72, 135.12, 175.89 (C=O).

Transformation of 14 to 3a. A mixture of **14** (60 mg, 0.17 mmol) and stannous chloride (140 mg) in glacial acetic acid (7 mL) was refluxed for 3 h. The mixture, on cooling, was treated with water and extracted with methylene chloride. The methylene chloride extract was washed with a 5% solution of sodium bicarbonate and dried over sodium sulfate, and the solvent was removed under vacuum to give 50 mg (91%) of **3a**, mp 124–125 °C (mixture melting point), after recrystallization from methanol.

Photolysis of 3,5-Diphenyl-3-(4-methylphenyl)-2(3*H*)-furanone (1b). Irradiation of a solution of **1b** (490 mg, 1.5 mmol) in benzene (200 mL) for 3 h (RPR, 3000 Å) and removal of the solvent under vacuum gave a solid, which was chromatographed over silica gel. Elution with a mixture (3:7) of benzene and petroleum ether gave 60 mg (12%) of the unchanged starting material (**1b**), mp 109–110 °C (mixture melting point). Further elution with a mixture (1:1) of benzene and petroleum ether gave 377 mg (84%) of **2b**, mp 105–106 °C: IR ν_{max} (KBr) 3075, 3050, 3020, 2930 (CH), 1660 (C=O), and 1585 (C=C) cm^{-1}; UV λ_{max} (methanol) 240 nm (ϵ 16 200), 335 (12 400); ^{1}H NMR (CDCl$_3$) δ 2.35 (3 H, s, methyl), and 7.48 (15 H, m, Ar and vinylic); mass spectrum, *m/e* (relative intensity) 298 (M$^+$, 100), 283 (M$^+$ – CH$_3$, 53), 221 (M$^+$ – C$_6$H$_5$, 24), 105 (C$_6$H$_5$CO$^+$, 20), and other peaks.

Anal. Calcd for C$_{22}$H$_{18}$O: C, 88.59; H, 6.04. Found: C, 88.62; H, 5.98.

In a repeat run, **1b** (600 mg, 1.8 mmol) in methanol (400 mL) was photolyzed for 4 h and worked up as in the earlier case to give 82 mg (14%) of recovered starting material (**1b**), mp 109–110 °C (mixture melting point), and 332 mg (60%) of **2b**, mp 105–106 °C (mixture melting point).

Irradiation of **1b** (326 mg, 1 mmol) in benzene (150 mL) containing acetophenone (60 mg, 0.5 mmol) for 3 h (RPR, 3500 Å), using a 2 mM naphthalene solution in benzene as filter, and removal of the solvent under vacuum gave a solid, which was chromatographed over silica gel. Elution with a mixture (1:1) of benzene and petroleum ether gave 150 mg (46%) of a mixture of the phenanthrofuranones **5b** and **6b** in a 3:2 ratio (by ^{1}H NMR). Further elution of the column with a mixture (4:1) of benzene and petroleum ether gave 98 mg (30%) of a mixture of the furanones **3b** and **4b** in a 3:2 ratio (by ^{1}H NMR).

The mixture of phenanthrofuranones **5b** and **6b** was separated by fractional crystallization from methanol–benzene mixture. The less soluble isomer was identified as 9-methyl-3-phenylphenanthro[9,10-*c*]furan-1(3*H*)-one (**6b**), mp 256–258 °C: IR λ_{max} (KBr) 3050, 3020, 2900 (CH), 1750 (C=O), 1630, 1600 (C=C) cm^{-1}; UV λ_{max} (methanol) 235 nm (ϵ 41 050), 252 (40 730), 261 (41 400), 282 (11 250), 312 (9270); ^{1}H NMR (CDCl$_3$) δ 2.30 (3 H, s, methyl), 6.18 (1 H, s, methine), 7.24 (10 H, m, Ar), 8.43 and 9.56 (2 H, m, H^7 and H^8 protons); mass spectrum, *m/e* (relative intensity) 324 (M$^+$, 24), 323 (M$^+$ – H, 18), 293 (M$^+$ – H – CO, 6), 218 (M$^+$ – H – COC$_6$H$_5$, 100), and other peaks.

Anal. Calcd for C$_{23}$H$_{16}$O$_2$: C, 85.19; H, 4.94; Found: C, 85.52; H, 4.77.

The more soluble isomer **5b** was isolated from the mother liquor through repeated column chromatography over silica gel and recrystallized from methanol, mp 264–265 °C: IR ν_{max} (KBr) 3060, 3020, 2960, 2900 (CH), 1750 (C=O), and 1620 (C=C) cm^{-1}; UV λ_{max} (methanol) 236 nm (ϵ 34 300), 253 (38 240), 262 (41 670); ^{1}H NMR (CDCl$_3$) δ 2.33 (3 H, s, methyl), 6.16 (1 H, s, methine), 7.28 (10 H, m, Ar), 8.26 and 9.33 (2 H, m, H^7 and H^8); mass spectrum, *m/e* (relative intensity) 324 (M$^+$, 25), 323 (M$^+$ – H, 21), 218 (M$^+$ – H – COC$_6$H$_5$, 100), and other peaks.

Anal. Calcd for C$_{23}$H$_{16}$O$_2$: C, 85.19; H, 4.94. Found: C, 85.47; H, 4.98.

Independent Synthesis of 4b. A mixture of α-bromodesoxybenzoin[10] (2.76 g, 10 mmol), potassium *p*-methylphenylacetate (1.89 g, 10 mmol), and 18-crown-6 (300 mg) in acetonitrile (50 mL) was refluxed for 1 h. The precipitated salt was filtered off and the solvent was removed under vacuum to give an oil, which was passed through a small silica gel column and recrystallized from methanol to give 2 g (58%) of benzoin *p*-methylphenylacetate (**10b**), mp 101–102 °C: IR λ_{max} (KBr) 3060, 3020, 2940, 2920 (CH), 1735 and 1680 (C=O), and 1590 (C=C) cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 2.32 (3 H, s, methyl), 3.76 (2 H, s, methylene), 6.86 (1 H, s, methine), and 7.6 (14 H, m, Ar).

Anal. Calcd for C$_{23}$H$_{20}$O$_3$: C, 80.23; H, 5.81. Found: C, 80.57; H, 6.02.

To a stirred solution of **10b** (340 mg, 1 mmol) in dry dimethyl sulfoxide (25 mL) was added sodium hydride (24 mg, 1 mmol) gradually, and the stirring was continued for 2 h at room temperature and then at 60–70 °C for another 10 min. The mixture was cooled, poured into cold water, and extracted with ether. The ether extract, after washing with dilute hydrochloric acid (2 N, 50 mL) and water, was dried over anhydrous sodium sulfate. Removal of the solvent gave 200 mg (61%) of 4,5-diphenyl-3-(4-methylphenyl)-2(5*H*)-furanone (**4b**), mp 127–128 °C, after recrystallization from methanol: IR ν_{max} (KBr) 3060, 3030, 2910 (CH), 1747 (C=O), 1630, and 1600 (C=C) cm^{-1}; UV λ_{max} (methanol) 224 nm (ϵ 24 550), 266 (11 650), 283 (12 730); ^{1}H NMR (CDCl$_3$) δ 2.33 (3 H, s, methyl), 6.23 (1 H, s, methine), and 7.39 (14 H, m, Ar).

Anal. Calcd for C$_{23}$H$_{18}$O$_2$: C, 84.66; H, 5.52. Found: C, 84.94; H, 5.37.

Preparation of the Phenanthrofuranone 6b. A solution of **4b** (50 mg, 0.15 mmol) in benzene (150 mL) was irradiated for 4 h (RPR, 3000 Å). Removal of the solvent under vacuum and recrystallization of the residue from methanol gave 37 mg (75%) of **6b**, mp 256–258 °C (mixture melting point).

Preparation of the Phenanthrofuranone 5b. A solution of **3b**[10] (50 mg, 0.15 mmol) in benzene (150 mL) was irradiated for 4 h (RPR, 3000 Å) and worked up by removal of the solvent under vacuum and recrystallization of the residue from methanol to give 40 mg (81%) of **5b**, mp 264–265 °C (mixture melting point).

Photolysis of 3,5-Diphenyl-3-(4-methoxyphenyl)-2(3*H*)-furanone (1c). A solution of **1c** (510 mg, 1.5 mmol) in benzene (200 mL) was irradiated for 3 h (RPR, 3000 Å). On removal of the solvent under vacuum, the residue was chromatographed over silica gel. Elution with a mixture (3:7) of benzene and petroleum ether gave 157 mg (31%) of unchanged starting material (**1c**), mp 92–93 °C (mixture melting point). Further elution with a mixture (1:1) of benzene and petroleum ether gave 300 mg (64%) of **2c**, mp 74–75 °C: IR ν_{max} (KBr) 3020, 2930, 2830 (CH), 1645 (C=O), 1580 (C=C); UV λ_{max} (methanol) 238 nm (ϵ 17 800), 336 (13 300); ^{1}H NMR (CDCl$_3$) δ 3.80 (3 H, s, methoxy), and 7.5 (15 H, m, Ar and vinylic).

Anal. Calcd for C$_{22}$H$_{18}$O$_2$: C, 84.08; H, 5.73. Found, C, 83.82; H, 5.61.

Irradiation of **1c** (510 mg, 1.5 mmol) in methanol (200 mL) under analogous conditions gave 152 mg (30%) of recovered starting material (**1c**), mp 92–93 °C (mixture melting point), and 300 mg (64%) of **2c**, mp 74–75 °C (mixture melting point). In a repeat run, a solution of **1c** (100 mg, 0.29 mmol) in benzene (150 mL) containing acetophenone (30 mg, 0.25 mmol) was irradiated for 3 h (RPR, 3500 Å), using a 2 mM naphthalene solution in benzene as filter. On removal of the solvent, the residue was chromatographed over silica gel. Elution with a mixture (1:1) of benzene and petroleum ether gave 40 mg (49%) of a mixture of phenanthrofuranones **5c** and **6c** in a 2:3 ratio (by ^{1}H NMR). Further elution of the column with a mixture (4:1) of benzene and petroleum ether gave 29 mg (29%) of a mixture of 2(5*H*)-furanones **3c** and **4c** in a 2:3 ratio (by ^{1}H NMR).

Independent Synthesis of 4c. A solution of α-bromodesoxybenzoin (2.76 g, 10 mmol), potassium *p*-methoxyphenylacetate (**9b**) (2.05 g, 10 mmol), and 18-crown-6 (250 mg) in acetonitrile (50 mL) was refluxed for 1 h. Removal of the precipitated salt and the solvent gave benzoin *p*-methoxyphenylacetate (**10d**), mp 108–109 °C, after recrystallization from methanol: IR ν_{max} (KBr) 3080, 3020, 3000, 2960, 2900 (CH), 1740 and 1690 (C=O), and 1590 (C=C) Cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 3.76 (2 H, s, methylene), 3.82 (3 H, s, methoxy), 6.75 (1 H, s, methine), and 7.5 (14 H, m, Ar).

Anal. Calcd for $C_{23}H_{20}O_4$: C, 76.67; H, 5.56. Found: C, 77.01; H, 5.80.

To a solution of **10d** (720 mg, 2 mmol) in dry dimethyl sulfoxide (50 mL) was added sodium hydride (48 mg, 2 mmol) while stirring. The stirring was continued at room temperature for 2 h and then at 60–70 °C for 10 min. Workup of the mixture as in the earlier case of **4b** gave 250 mg (35%) of **4c**, mp 126–127 °C, after recrystallization from methanol: IR ν_{max} (KBr) 3060, 3035, 3000, 2960 (CH), 1750 (C=O), and 1600 (C=C) cm^{-1}; UV λ_{max} (methanol) 228 nm (ϵ 21 970), 270 (10 200), 300 (9550); ^{1}H NMR (CDCl$_3$) δ 3.81 (3 H, s, methoxy), 6.20 (1 H, s, methine), and 7.13 (14 H, m, Ar).

Anal. Calcd for $C_{23}H_{18}O_3$: C, 80.70; H, 5.26. Found: C, 80.27; H, 5.68.

Preparation of the Phenanthrofuranone 6c. A solution of **4c** (50 mg, 0.146 mmol) in benzene (150 mL) was irradiated for 4 h (RPR, 3000 Å). Removal of the solvent under vacuum and recrystallization of the residue from methanol gave 42 mg (85%) of **6c**, mp 216–218 °C; IR ν_{max} (KBr) 3070, 3030, 2900 (CH), 1750 (C=O), and 1600 (C=C) cm^{-1}; UV λ_{max} (methanol) 242 nm (ϵ 40 430), 248 (39 900), 262 (29 250, sh), 290 (7980), 322 (6900); ^{1}H NMR (CDCl$_3$) δ 3.60 (3 H, s, methoxy), 6.20 (1 H, s, methine), 7.41 (10 H, m, Ar), 8.43 and 9.33 (2 H, m, H^7 and H^8).

Anal. Calcd for $C_{23}H_{16}O_3$: C, 81.18; H, 4.71. Found: C, 81.25; H, 4.52.

Preparation of the Phenanthrofuranone 5c. A solution of **3c**[10] (50 mg, 0.146 mmol) in benzene (150 mL) was irradiated for 4 h (RPR, 3000 Å) and the solvent was removed under vacuum to give 40 mg (81%) of **5c**, mp 223–225 °C, after recrystallization from methanol: IR ν_{max} (KBr) 3060, 3020, 3000, 2970, and 2940 (CH), 1740 (C=O), 1610, and 1590 (C=C) cm^{-1}; UV λ_{max} (methanol) 243 nm (ϵ 27 330), 260 (29 030), 278 (12 300), 322 (10 170); ^{1}H NMR (CDCl$_3$) δ 4.0 (3 H, s, methoxy), 6.60 (1 H, s, methine), 7.55 (10 H, m, Ar), 8.66 and 9.23 (2 H, m, H^7 and H^8).

Anal. Calcd for $C_{23}H_{16}O_3$: C, 81.18; H, 4.71. Found: C, 81.42; H, 4.93.

Photolysis of 3-(4-Cyanophenyl)-3,5-diphenyl-2(3*H*)-furanone (1d). A solution of **1d** (337 mg, 1 mmol) in benzene (200 mL) was irradiated for 3 h (RPR, 3000 Å). The solvent was removed under vacuum and the residue was chromatographed on silica gel. Elution with a mixture (2:3) of benzene and petroleum ether gave 34 mg (10%) of recovered starting material **1d**, mp 114–115 °C (mixture melting point). Futher elution with a mixture (1:1) of benzene and petroleum ether gave 260 mg (85%) of **2d**, mp 113–114 °C, after recrystallization from methanol: IR ν_{max} (KBr) 3050, 3020 (CH), 2220 (C≡N), 1650 (C=O), and 1585 (C=C) cm^{-1}; UV λ_{max} (methanol) 250 nm (ϵ 22 650), 268 (16 650), 296 (15 350); ^{1}H NMR (CDCl$_3$) δ 7.6 (m, Ar and vinylic).

Anal. Calcd for $C_{22}H_{15}NO$: C, 85.44; H, 4.85; N, 4.53. Found: C, 85.01; H, 4.92; N, 4.67.

Irradiation of **1d** (337 mg, 1 mmol) in methanol (200 mL) under analogous conditions gave 30 mg (9%) of recovered starting material (**1d**), mp 114–115 °C (mixture melting point), and 270 mg (87%) of **2d**, mp 113–114 °C (mixture melting point). In a repeat experiment, a solution of **1d** (300 mg, 0.9 mmol) in benzene (300 mL) was irradiated for 3 h (RPR, 3500 Å), using a 2 mM naphthalene solution in benzene as filter. Removal of the solvent gave a residue, which was chromatographed over silica gel. Elution with a mixture (2:3) of benzene and petroleum ether gave 120 mg (40%) of the dimer **7d**, mp >360 °C: IR ν_{max} (KBr) 3060, 3025 (CH), 2220 (C≡N), and 1760 (C=O); UV λ_{max} (acetonitrile) 234 nm (ϵ 40 570, sh), 270 (5620); ^{1}H NMR (CDCl$_3$) δ 5.07 (2 H, s, methine), 7.21 (28 H, m, Ar); mass spectrum, *m*/*e* (relative intensity) 674 (M$^+$, 2), 337 (M$^+$/2, 11), 336 (M$^+$/2 – H, 43), 231 (M$^+$/2 – H – COC$_6$H$_5$, 100), and other peaks.

Anal. Calcd for $C_{46}H_{30}N_2O_4$: C, 81.90; H, 4.45; N, 4.15. Found: C, 81.87; H, 4.35; N, 3.85.

Further elution of the column with a mixture (3:2) of benzene and petroleum ether gave 55 mg (18%) of the phenanthrofuranone **5d**, mp 265–267 °C, after recrystallization from methanol: IR ν_{max} (KBr) 3080, 3050, 3010 (CH), 2220 (C≡N), 1740 (C=O), and 1595 (C=C) cm^{-1}; UV λ_{max} (methanol) 233 nm (ϵ 37 630), 250 (38 650), 260 (35 570, sh), 284 (10 050, sh), 320 (10 200); ^{1}H NMR (Me$_2$SO-*d*$_6$) δ 7.0 (11 H, m, Ar and methine), 8.3 and 8.8 (2 H, m, H^7 and H^8).

Anal. Calcd for $C_{23}H_{13}NO_2$: C, 82.39; H, 3.88; N, 4.18. Found: C, 81.91; H, 3.52; N, 4.15.

Further elution of the column with a mixture (4:1) of benzene and petroleum ether gave 48 mg (16%) of **3d**, mp 177–178 °C (mixture melting point) (lit.[10] mp 178–179 °C).

Preparation of the Phenanthrofuranone 5d. A solution of **3d** (50 mg, 0.15 mmol) in benzene (150 mL) was irradiated for 4 h (RPR, 3000 Å). Removal of the solvent under vacuum and recrystallization of the residue from methanol gave 35 mg (71%) of **5d**, mp 265–267 °C (mixture melting point).

Photolysis of 3-(4-Chlorophenyl)-3,5-diphenyl-2(3*H*)-furanone (1e). A solution of **1e** (200 mg, 0.58 mmol) in benzene (200 mL) was irradiated for 4 h (RPR, 3000 Å). Removal of the solvent under vacuum and recrystallization of the residue from petroleum ether gave 160 mg (82%) of **2e**, mp 106–107 °C: IR ν_{max} (KBr) 3040, 3010 (CH), 1645 (C=O)) and 1580 (C=C) cm^{-1}; UV λ_{max} (methanol) 232 nm (ϵ 16 800), 312 (10 900); ^{1}H NMR (CDCl$_3$) δ 7.55 (m, Ar and vinylic).

Anal. Calcd for $C_{21}H_{15}OCl$: C, 79.25; H, 4.72. Found, C, 79.53; H, 4.86.

Irradiation of **1e** (100 mg, 0.29 mmol) in methanol (150 mL) under analogous conditions gave 75 mg (76%) of **2e**, mp 106–107 °C (mixture melting point). In a repeat experiment, a solution of **1e** (150 mg, 0.44 mmol) in benzene (450 mL) containing acetophenone (60 mg, 0.5 mmol) was irradiated for 3 h (RPR, 3500 Å). The residue, after removal of the solvent, was chromatographed over silica gel. Elution with a mixture (2:3) of benzene and petroleum ether gave 80 mg (53%) of the dimer **7e**, mp >360 °C: IR ν_{max} (KBr) 3050, 3020 (CH), 1760 (C=O), and 1595 (C=C) cm^{-1}; UV λ_{max} (acetonitrile) 232 nm (ϵ 22 950 sh), 260 (6120); ^{1}H NMR (CDCl$_3$) δ 5.0 (2 H, s, methine), 7.16 (28 H, m, Ar).

Anal. Calcd for $C_{44}H_{30}Cl_2O_4$: C, 76.30; H, 4.33. Found: C, 76.33; H, 3.94.

Futher elution of the column with a mixture (3:2) of benzene and petroleum ether gave 20 mg (13%) of the phenanthrofuranone **5e**, mp 262 °C, after recrystallization from methanol: IR ν_{max} (KBr) 3060, 3020 (CH), 1740 (C=O), 1590 (C=C) cm^{-1}; UV λ_{max} (methanol) 234 nm (ϵ 27 870), 248 (25 850, sh), 260 (29 300), 278 (9770, sh), 310 (8620); ^{1}H NMR (CDCl$_3$) δ 6.70 (1 H, s, methine), 7.66 (10 H, m, Ar), 8.75 and 9.33 (2 H, m, H^7 and H^8).

Anal. Calcd for $C_{22}H_{13}ClO_2$: C, 76.74; H, 3.76. Found: C, 76.43; H, 3.54.

Futher elution of the column with a mixture (4:1) of benzene and petroleum ether gave 20 mg (13%) of the 2(5*H*)-furanone **3e**, mp 173–174 °C: IR ν_{max} (KBr) 3050, 3020 (CH), 1750 (C=O), and 1590 (C=C) cm^{-1}; UV λ_{max} (methanol) 220 nm (ϵ 25 380), 260 (11 150), 290 (1000); ^{1}H NMR (CDCl$_3$) δ 6.26 (1 H, s, methine), 7.55 (14 H, m, Ar).

Anal. Calcd for $C_{22}H_{15}O_2Cl$: C, 76.30; H, 4.34. Found: C, 76.66; H, 4.08.

Independent Synthesis of 3e. To an ether solution of 4-chlorodesoxybenzoin (2.3 g, 10 mmol in 25 mL) was added a solution of bromine (1.6 g, 10 mmol) in ether (10 mL) with stirring (30 min), and the reaction mixture was quenched by the addition of a 1% aqueous solution of sodium thiosulfate. The organic layer was washed with water and dried over anhydrous magnesium sulfate, and the solvent was removed under vacuum to give a nearly quantitative yield of 4-chlorodesyl bromide. The crude bromo ketone was taken up in acetonitrile (50 mL) and refluxed for 2 h after adding potassium phenylacetate (1.75 g, 10 mmol) and 18-crown-6 (300 mg). Workup of the mixture as in the earlier cases gave 2.0 g (55%) of 4-chlorobenzoin phenylacetate (**10f**), mp 64–65 °C: IR ν_{max} (KBr) 3090, 3060, 3030 and 2920 (CH), 1735 and 1695 (C=O), 1590 (C=C) cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 3.83 (2 H, s, methylene), 6.80 (1 H, s, methine), 7.55 (14 H, m, Ar). Anal. Calcd for $C_{22}H_{17}O_3Cl$: C, 72.53; H, 4.67. Found: C, 72.26; H, 4.41.

To a solution of **10f** (728 mg, 2 mmol) in dry dimethyl sulfoxide (50 mL) was added sodium hydride (48 mg, 2 mmol), and the mixture was stirred at 20 °C for 2 h and later at 60–70 °C for 10 min. Workup as in earlier cases gave 350 mg (50%) of **3e**, mp 173–174 °C (mixture melting point).

Preparation of the Phenanthrofuranone 5e. A solution of **3e** (50 mg, 0.14 mmol) in benzene (150 mL) was irradiated for 4 h (RPR, 3000 Å) and removal of the solvent under vacuum gave 35 mg (71%) of **5e**, mp 262–264 °C (mixture melting point).

Low-Conversion Photolysis of 1e. Low-conversion photolysis experiments were carried out with **1e** as a representative case. The general procedure was to dissolve 35 mg (0.01 mmol) of **1e** in benzene (20 mL) containing acetophenone (25 mg, 0.21 mmol) and irradiate the resulting solution at 3500 Å (filtered through a 2 mM solution of naphthalene in benzene). The photolysis was conducted for three different time periods, viz. 10, 20, and 40 min. In each case the solvent was removed under vacuum and the residue was dissolved completely in CDCl$_3$ for ^{1}H NMR. The relative concentrations (%) of the starting material and the photoproducts as obtained from ^{1}H NMR are given below. Within the limit of our detection, no evidence could be obtained for the formation of the isomer, 3-(4-chlorophenyl)-4,5-diphenyl-2-(5*H*)-furanone (<5%).

irradn time, in	startg matl (1e)	3e	5e	7e
10	66	22	not observed	11
20	20	43	8	29
40	12	35	12	41

Laser Flash Photolysis. For laser flash photolysis, use was made of a computer-controlled set-up described elsewhere.[23] The pulsed laser sources were Lambda-Physik EMG 101 excimer (248 and 308 nm, ~20 ns), Molectron UV-400 nitrogen (337.1 nm, ~8 ns), and Quanta-Ray DCR-1 Nd-YAG (third harmonic, 355 nm, ~6 ns). The laser intensities were attenuated and kept in the range 2–10 mJ/pulse. For transient spectra, a flow cell was used. Deoxygenation of solutions was effected by saturation with argon.

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Fumarase-Catalyzed Synthesis of L-*threo*-Chloromalic Acid and Its Conversion to 2-Deoxy-D-ribose and D-*erythro*-Sphingosine

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This paper describes the use of pig heart fumarase (E.C. 4.2.1.2) as a catalyst in the multigram synthesis of L-*threo*-chloromalic acid (1) (≥99.5% enantiomeric excess) on 50-g scale. L-*threo*-Fluoromalic acid has been synthesized in a coupled enzymic system from difluorofumaric acid. Compound 1 serves as starting material for syntheses of 2-deoxy-D-ribose and D-*erythro*-sphingosine.

Introduction

Much of the current effort in developing applications of enzymes to enantioselective organic synthesis has focused on classes of enzymes with broad substrate specificity: lipases, esterases, amidases, and related hydrolases.[1-3] These enzymes are indisputably valuable but have certain disadvantages, among which is often imperfect enantioselectivity. The standards in enantioselective synthesis are now very high: for most applications, an enantiomeric excess (ee) in an enantioselective step of less than 90% is essentially useless, and values of ee >99% are very desirable.[4] It is often difficult to achieve broad substrate selectivity and high enantioselectivity simultaneously. This difficulty poses a strategic question for the synthetic chemist: Is it better to use a structurally "efficient" intermediate with modest enantiomeric purity in a synthetic scheme—that is, an intermediate that can be generated easily and converted to the desired product by using an efficient synthetic sequence (but with imperfect overall control of enantiomeric purity)—or is it better to use a less "efficient" intermediate having higher enantiomeric purity? There is no general answer to this question, but it does pose a related question in enzyme-catalyzed synthesis: What are the relative values as catalysts of enzymes with broad substrate specificity and moderate enantioselectivity relative to enzymes with narrow substrate specificity and high enantioselectivity? This paper explores the utility in organic synthesis of a representative enzyme—fumarase—in the second catagory.

Fumarase (E.C. 4.2.1.2) generates a chiral center(s) from an achiral substrate by stereospecific hydration of a carbon–carbon double bond.[5] In vivo, fumarase catalyzes the reversible hydration of fumarate to L-malate; it is used in a commercial synthesis of this substance (eq 1).[3] We demonstrate here that it also is a useful catalyst for conversion of chlorofumaric acid to L-*threo*-chloromalic acid (1) (eq 2); its broader application in organic synthesis is, however, limited, because only a few analogs of fumaric

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