matography using an 80:20 mixture of hexane/ethyl acetate. *endo*-Bicyclo[2.2.1]hept-2-en-5-yl 2,5-dimethyl-4-oxazolyl ketone (**8**) was obtained as a white solid: mp 66–68°C; yield, 0.070 g (41%); IR (CCl_4) 5.90 (s) 13.9 (m) μm; ^1H NMR δ 1.10–4.00 (m, 7 H), 2.50 (s, 3 H), 2.56 (s, 3 H), 5.67–6.27 (q, 2 H).

Anal. Calcd for $C_{13}H_{15}NO_2$: C, 71.86; H, 6.96; N, 6.45. Found: C, 71.97; H, 7.26; N, 6.29.

5-(Bicyclo[2.2.1]hept-2-en-5-yl)-2-methyl-4-acetyloxazole (17) was obtained as an oil: yield, 0.050 g (29%); IR (CCl_4) 5.93 (s), 14.1 (w) μm; ^1H NMR δ 1.10–4.16 (m, 7 H), 2.33 (s, 3 H), 2.46 (s, 3 H), 5.60–6.27 (q, 2 H).

Anal. Calcd for $C_{13}H_{15}NO_2$: C, 71.86; H, 6.96; N, 6.45. Found: C, 68.10, 72.64, 73.18; H, 6.64, 7.99, 7.76; N, 6.07, 5.26, 4.07.

Irradiation of 16. Degassed solutions of 2*H*-azirine **16** in CD_3CN were irradiated at 254, 300, and 350 nm for long periods with no significant change as monitored by ^1H NMR. Under comparable conditions at 254 nm isoxazole **6** was consumed to the extent of ca. 85%.

Quantum Yields. Quantum yields were determined in the Rayonet reactor at 253.7 and 300 nm in degassed 1.0 M solutions in CD_3CN.[19] The rate of disappearance of ketone **6** was measured by ^1H NMR or absorption spectroscopy and assumed to be equal to the rate of formation of oxetane **2d** and 2*H*-azirine **16** because no other productts (±5%) were seen. Light intensities were monitored by use of 0.15 M potassium ferric oxalate[20] ($\phi^{300\mathrm{nm}}$ = 1.24) and by 4-acetyl-3,5-dimethylisoxazole[21] ($\phi^{254\mathrm{nm}}{}_K$ = 0.18 ± 0.02). Potassium ferric oxalate was freshly recrystallized before use, and all manipulations with actinometer solutions were done in the dark. After irradiation, an aliquot of the photolysate was added to a premixed solution of 2 mL of 0.1% *o*-phenanthroline, 0.5 mL of buffer, and 0.9 mL of 0.1 M H_2SO_4. After 1 h in the dark the concentration of Fe^{2+} was calculated from the absorbance of the complex at 540 nm.

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Registry No. 1 (R = OH), 1195-12-6; **2a**, 110773-83-6; **2b**, 110773-84-7; **2c**, 110773-85-8; **2d**, 110773-86-9; **2e**, 110773-87-0; **2f**, 110773-88-1; **3**, 110773-89-2; **4**, 110773-90-5; **5**, 110773-91-6; *endo*-**6**, 110773-92-7; *exo*-**6**, 110773-93-8; *endo*-**7**, 110773-94-9; *exo*-**7**, 110773-95-0; **8**, 110773-96-1; **9**, 110773-97-2; **12**, 110773-98-3; **13**, 54593-26-9; **14**, 110773-99-4; **16**, 110774-00-0; **17**, 110796-29-7; furan, 110-00-9; thiophene, 110-02-1; *N*-methylpyrrole, 96-54-8; 3-formyl-5-methylisoxazole, 24068-54-0; cyclopentadiene, 542-92-7.

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(19) For more details, see: Van Arnum, S. D. Thesis, Rutgers University, 1987.

(20) Hatchard, C. G.; Parker, G. A. *Proc. R. Soc. London, A.* **1956**, *235*, 518.

(21) Scimone, A. A., thesis, Rutgers University, 1987.

Photochemical and Thermal Transformations of 3-Benzyl-2(3*H*)-furanones and Related Substrates[1]

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Photochemical and thermal transformations of several 2(3*H*)-furanones are reported. Steady-state irradiations of 3-benzyl-3,5-diphenyl-2(3*H*)-furanone (**1a**) in benzene or methanol, for example, gave a mixture of 2,3,5-triphenylfuran (**3a**) (8–9%) and 1,3,5-triphenylbut-3-en-1-one (**6a**) (26–34%), along with 34–37% recovery of the unchanged starting material. Similar results were obtained with 3-benzyl-3-(4-methylphenyl)-5-phenyl-2-(3*H*)-furanone (**1b**) and 3-benzyl-3-(4-methoxyphenyl)-5-phenyl-2(3*H*)-furanone (**1c**) under analogous conditions. Upon direct irradiation, 3,3-dibenzyl-5-phenyl-2(3*H*)-furanone (**1d**), however, gave only 3-benzyl-1,4-diphenylbut-3-en-1-one (**6d**) (80–83%), whereas 3-benzyl-3-phenylphenanthro[9,10-*b*]furan-2(3*H*)-one (**1e**) gave only 2,3-diphenylphenanthro[9,10-*b*]furan (**3e**) (15–21%). On the other hand, 3-benzoyl-3,5-diphenyl-2(3*H*)-furanone (**1f**) gave only the bis lactone **10a** (72–75%) under direct photolysis. The bis lactones **10a–c** and the rearranged 5-benzyl-3,5-diaryl-2(5*H*)-furanones **9a–d** were the major products in the course of sensitized irradiation of **1a–d** in the presence of acetophenone in benzene. The thermolysis of **1a–d** also led to the formation of the rearrangement products **9a–d** in high yields (60–80%). Possible mechanisms of these various photochemical and thermal reactions are discussed in terms of singlet-mediated decarbonylation, triplet-sensitized homolysis of the benzyl-to-furanone bond and probable thermal [1,3]-sigmatropic shift of the benzyl group. The laser pulse photoexcitation (337.1 nm) of benzophenone in the presence of **1a–d** in benzene of acetonitrile produces the short-lived triplets of the 2(3*H*)-furanones (τ_T = 0.5–3.0 μs), which subsequently undergo bond cleavage leading to furanoxy radicals. The spectral and kinetic features of the triplets and the radicals are presented.

Introduction

Photochemical and thermal transformations of several unsaturated lactones have been extensively investigated.[3-29] It has been observed that these lactones undergo a of phototransformations, namely, decarbonylation,[4,5,9,24,26]

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(2) (a) University of Notre Dame. (b) Indian Institute of Technology. (c) Visiting undergraduate research student from the University of Waterloo, Waterloo, Ontario.

(3) Rao, Y. S. *Chem. Rev.* **1976**, *76*, 625–694.

(4) Yogev, A.; Mazur, Y. *J. Am. Chem. Soc.* **1965**, *87*, 3520–3521.

(5) Gutsche, C. D.; Oude-Alink, B. A. M. *J. Am. Chem. Soc.* **1968**, *90*, 5855–5861.

(6) Krull, I. S.; Arnold, D. R. *Tetrahedron Lett.* **1969**, *1247*–1249.

(7) Rio, G.; Hardy, J.-C. *Bull. Soc. Chim. Fr.* **1970**, 3578–3584.

(8) Rio, G.; Hardy, J.-C. *Bull. Soc. Chim. Fr.* **1970**, 3572–3578.

(9) Chapman, O. L.; McIntosh, C. L. *J. Chem. Soc., Chem. Commun.* **1971**, *383*–384.

(10) Ohga, K.; Matsuo, T. *J. Org. Chem.* **1974**, *39*, 106–108.

(11) Skorianetz, W.; Ohloff, G. *Helv. Chim. Acta* **1975**, *58*, 1272–1275.

(12) Padwa, A.; Dehm, D. *J. Am. Chem. Soc.* **1975**, *97*, 4779–4781.

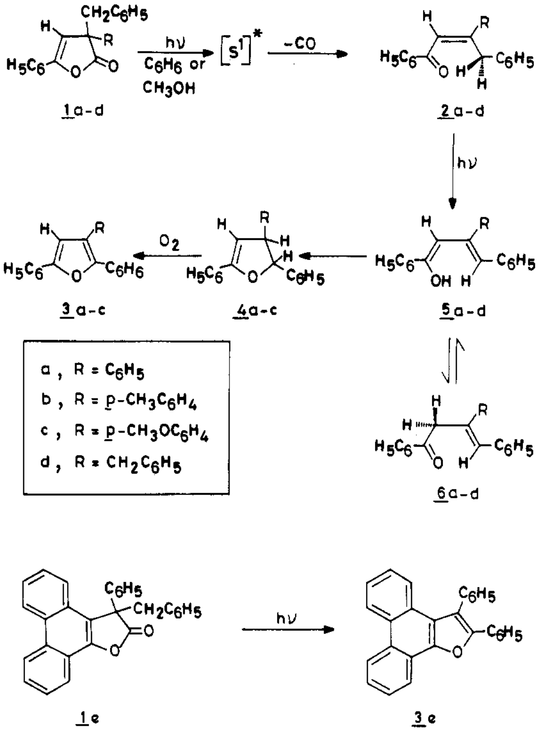
(13) Ogha, K.; Matsuo, T. *Bull. Chem. Soc. Jpn.* **1976**, *49*, 1590–1594.

decarboxylation,[6] solvent addition to the double bond,[10,12,16,17] migration of aryl substituents,[17,26,29] and dimerization.[13,29] Thus, in the case of 2(3*H*)-furanones, it has been noted that a critical requirement for decarbonylation is the presence of a double bond adjacent to the ether oxygen,[9] which can stabilize the diradical produced by cleavage of the acyl–oxygen bond. Photochemical reactions observed in several related systems are similar. In comparison, the thermal transformations of these substrates lead to decarbonylated products[20,21,26] and, in some cases, rearrangement products arising through [1,3]-sigmatropic shifts of substituent groups.[22,25]

In some recent publications,[26-29] we have reported on 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 major photoreaction pathways of these 2(3*H*)-furanones include singlet-mediated decarbonylation to give α,β-unsaturated carbonyl compounds, singlet-mediated cyclization involving adjacent phenyl substituents to give 4a,4b-dihydrophenanthrene derivatives, and triplet-mediated rearrangement to give 2(5*H*)-furanones. On the basis of product analysis and laser flash photolysis studies, we have determined the migratory aptitudes and migrating rates of the various aryl groups in the sensitized rearrangement reactions.

In the present study, we have examined the photochemical and thermal transformations of a few 2(3*H*)-furanones containing a benzyl or benzoyl group at the 3-position. Interestingly, in addition to decarbonylation under direct excitation, we have observed facile photochemical cleavage of the benzyl and benzoyl groups leading to furanoxy radicals, characterized by sharp and well-defined absorption spectral features. The furanones we have examined include 3-benzyl-3,5-diphenyl-2(3*H*)-furanone (**1a**), 3-benzyl-3-(4-methyl-phenyl)-5-phenyl-2(3*H*)-furanone (**1b**), 3-benzyl-3-(4-methoxyphenyl)-5-phenyl-2-(3*H*)-furanone (**1c**). 3,3-dibenzyl-5-phenyl-2(3*H*)-furanone (**1d**), 3-benzyl-3-phenylphenanthro[9,10-*b*]furan-2(3*H*)-one (**1e**), and 3-benzoyl-3,5-diphenyl-2(3*H*)-furanone (**1f**).

Scheme I



Results and Discussion

(1) Preparative Photochemistry and Product Identification. The photolysis of solutions of 2(3*H*)-furanone **1a** in benzene or methanol (RPR 3000 Å, Rayonet) gave a mixture of 2,3,5-triphenylfuran (**3a** 8–9%), 1,3,4-triphenylbut-3-en-1-one (**6a**, 20-26%), and the unreacted starting material (**1a**, 34–37%). In contrast, the irradiation in benzene (RPR 3500 Å, Rayonet) using acetophenone as sensitizer gave a mixture of the rearranged lactone **9a** (35%) and the bis lactone **10a** (27%), along with a 25% recovery of the unchanged starting material.

The irradiation of **1b** and **1c** in benzene and methanol under analogous conditions, gave the corresponding furan derivatives **3b** (6–13%) and **3c** (8–11%) and the butenone derivatives **6b** (21–31%) and **6c** (24–25%), respectively. The sensitized irradiation in benzene in the presence of acetophenone, however, gave the corresponding rearranged products **9b** (50%) (48%) and the bis lactones **10b,c** (7%), along with 25% recovery of the starting material in each case. The irradiation of **1d** in benzene or methanol gave **6d** (80–83%) as the only product; the sensitized irradiation in the presence of acetophenone also gave only one product, viz., the 2(5*H*)-furanone **9d** (23%) along with a 58% recovery of the starting material. The irradiation of **1e** in methanol or benzene gave **3e** as the only product, while the 3-benzoyl derivative **1f** under direct photolysis in methanol or benzene or under acetophenone sensitization in benzene gave only the bis lactone **10a** (72–74%).

The formation of the various photoproducts in the irradiation of the 2(3*H*)-furanones in benzene or methanol can be understood in terms of the pathways shown in Scheme I. The initial excitation of the furanones to the corresponding singlet excited states results in decarbonylation to the intermediate α,β-unsaturated ketones **2a–d**, which could not be isolated under our reaction conditions. The α,β-unsaturated ketones **2a–d**, having a methylene group γ to the carbonyl group possibly undergo photochemical γ-hydrogen abstraction to give the enolic intermediates **5a–d**, which in turn can tautomerize to the β,γ-unsaturated ketones **6a–d**. Alternatively, the enol inter-

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[14] Kosugi, K.; Sekiguchi, S.; Sekita, R.; Uda, H. *Bull. Chem. Soc. Jpn.* **1976**, *49*, 520–528.

[15] Padwa, A.; Ku, A.; Sato, E. *Tetrahedron Lett.* **1976**, 2409–2412.

[16] Padwa, A.; Brookhart, T.; Dehm, D.; West, G.; Wubbels, G. *J. Am. Chem. Soc.* **1977**, *99*, 2347–2348.

[17] Padwa, A.; Brookhart, T.; Dehm, D.; Wubbels, G. *J. Am. Chem. Soc.* **1978**, *100*, 8247–8259.

[18] Zimmer, H.; Downs, B. W. *J. Heterocycl. Chem.* **1978**, *15*, 703–704.

[19] Utrilla, R. M.; Miranda, M. A. *Tetrahedron* **1981**, *37*, 2111–2114.

[20] Blat, A. H. *J. Org. Chem.* **1950**, *15*, 869–872.

[21] Japp, F. R.; Klingemann, F. *J. Chem. Soc.* **1980**, *57*, 662–713.

[22] Wiberg, K. B.; Hutton, T. W. *J. Am. Chem. Soc.* **1954**, *76*, 5367–5371.

[23] Oude-Alink, B. A. M.; Chan, A. W. K.; Gutsche, C. D. *J. Org. Chem.* **1973**, *38*, 1993–2001.

[24] Tokumaru, K.; Sakuragi, H.; Takahashi, T. *Chem. Lett.* **1972**, 957–962.

[25] Woodward, R. B.; Hoffmann, R. *The Conservation of Orbital Symmetry*; Academic: New York, 1970.

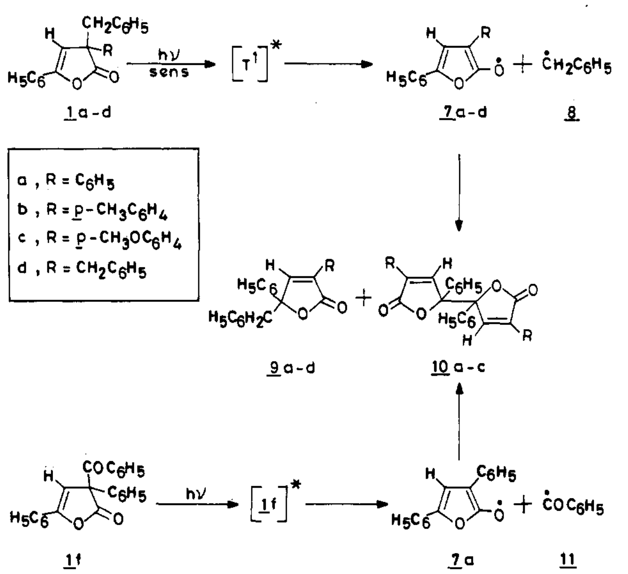
[26] Lohray, B. B.; Kumar, C. V.; Das, P. K.; George, M. V. *J. Am. Chem. Soc.* **1984**, *106*, 7352–7359.

[27] Bhattacharyya, K.; Das, P. K.; Fessenden, R. W.; George, M. V.; Gopidas, K. R.; Hug, G. L. *J. Phys. Chem.* **1985**, *89*, 4164–4166.

[28] Davis, H. G.; Lohray, B. B.; Gopidas, K. R.; Kumar, C. V.; Das, P. K.; George, M. V. *J. Org. Chem.* **1985**, *50*, 3685–3692.

[29] (a) Gopidas, K. R.; Lohray, B. B.; Rajadurai, S.; Das, P. K.; George, M. V. *J. Org. Chem.* **1987**, *52*, 2831–2838. (b) Our inability to isolate fragmentation-derived products (i.e., **9c** and **10c**) in the course of preparative photochemistry of **1c** under direct excitation is probably due to the fact that their relative amounts in the photolysates are small. Although the quantum yield of fragmentation is nonnegligible (0.1) in the case of **1c**, note that the photolysis proceeds only to 50% consumption of the starting substrate; the latter is due to the screening of the light by accumulated photoproducts, particularly, the initial decarbonylation product (**2c**).

Scheme II



mediates (**5a–c**) can undergo photocyclization to give the corresponding dihydrofuran derivatives **4a–c**, which can undergo subsequent air oxidation under the conditions of workup, to give the furan derivatives **3a–c**. Similar photochemical isomerization of α,β-unsaturated ketones to β,γ-unsaturated ketones and related products is well documented in the literature.[30,31] It may be pointed out here that our attempts to bring about the cyclization of the enone **6a** to the corresponding dihydrofuran **4a** (or furan **3a**) by heating in toluene in the presence of *p*-toluenesulfonic acid were unsuccessful. It is therefore likely that the cyclization of the enols **5a–c** to the corresponding dihydrofuran derivatives **4a–c** (or the furans **3a–c**) proceeds under photoexcitation. The absence of any β,γ-unsaturated ketone in the case of **1e** may be due to the fact that its formation reduces the aromatic stabilization of the phenanthrene system. However, the reasons for the absence of any furan derivative **3d** in the case of **1d** are not very clear.

The formation of 2(5*H*)-furanones **9a–d** as well as bis lactones **10a–c** in acetophenone sensitization experiments of **1a–d** can be explained by the pathways shown in Scheme II. The triplets of these substrates produced by excitation transfer from acetophenone triplet undergo cleavage at the C-3 position to give benzyl and furanoxy radicals. That such a cleavage occurs to produce furanoxy radicals is confirmed by laser flash photolysis studies (see later). The recombination of the radicals lead to the formation of either the starting materials **1a–d** or the rearranged products **9a–d**. The coupling of two furanoxy radicals at the 5-position leads to the formation of bis lactones **10a–c**. One would also expect the coupling of benzyl radicals to produce bibenzyl. In fact, a small amount (7%) of bibenzyl could be isolated in the acetophenophenone-sensitized photolysis of **1c**; this is in support of the pathways shown in Scheme II. The formation of the bis lactone **10a** in the photolysis of **1f** can also be explained in a terms of singlet or triplet-mediated cleavage of the benzoyl group.

(2) Thermal Transformations of 2(3*H*)-Furanones 1a–d. The thermolysis of **1a** in a sealed tube at 250 °C for 2 h led to the formation of the isomeric lactone **9a** in 60% yield. Similarly, the thermolysis of **1b–d** under analogous conditions gave the corresponding 2(5*H*)-furanones **9b–d** in 70–80% yields. The formation of the rearranged products **9a–d** in these reactions may be via a thermal [1,3]-sigmatropic shift with inversion of configuration at the migrating center,[25] or through a radical pathway. However, in the absence of products that could arise through radical coupling, namely, **10a–c**, a radical pathway seems less likely.

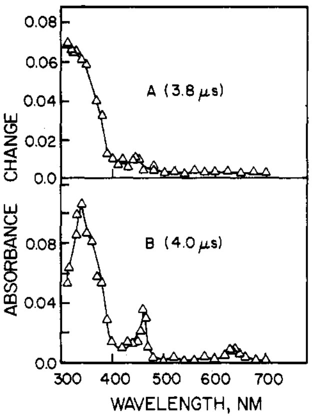


Figure 1. Photoproduct absorption spectra observed upon 308-nm laser flash photolysis of (A) 21 mM **1a** and (B) 25 mM **1c** in benzene. The times after laser flash at which the spectra were recorded are shown in the figures.

(3) Laser Flash Photolysis Studies. The lowest energy absorption band systems of 2(3*H*)-furanones **1a–d** in benzene extend up to 320 nm, and it is possible to excite them directly by 308 nm laser pulses (Xe/Cl excimer) using relatively concentrated solutions (≥15 mM). Also, at high concentrations (20–30 mM), **1a–d** do not absorb significantly at 337.1 nm (i.e., the wavelength of nitrogen laser pulses); thus, sensitization experiments are feasible in which benzophenone (BP, donor) can be exclusively photoexcited in the presence of the substrates without having the complication of partial screening of laser photons by the latter. We have not attempted to study the quenching of BP triplet (E_T = 69 kcal/mol),[32] by **1a–d** because of the strong spectral and temporal overlap of the triplet–triplet absorption of the aromatic ketone with the transient absorptions of the triplets of **1a–d** and triplet-derived furanoxy radicals as well as the delayed doublet-doublet emission of the latter (see later). However, since the triplet energy of **1a–d** would be close to that of styrene ($E_T \simeq$ 62 kcal/mol),[32] it is expected that the quenching of BP triplet by **1a–d** should occur in a diffusion-controlled manner. As a matter of fact, in a previous study,[26] we have found that the rate constant for the quenching of BP triplet by 3,3,5-triphenyl-2(3*H*)-furanone is 2.1×10^9 M^{-1} s^{-1} (in benzene).

Upon direct laser pulse excitation (308 nm), **1a–c** in benzene produce weak absorbance changes due to photoproducts (λ_{max} = 320–350 nm) which do not show any sign of decay on our longest time scale (~130 μs). The photoproduct absorption spectra in the case of **1a** and **1c** are presented in Figure 1. **1b** behaves similarly as **1a**. It is evident that in the case of **1c**, a second long-lived transient product exhibits its maxima at 460 and 640 nm (Figure 1B). The latter is identified as the furanoxy radical **7c** (see below). The "permanent" photoproducts absorbing at 310–360 nm are commonly observed in the course of direct laser excitation of aryl-substituted 2(3*H*)-furanones in

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(30) Jorgenson, M. J.; Yang, N. C. *J. Am. Chem. Soc.* **1963**, *85*, 1698–1699.

(31) Yang, N. C.; Jorgenson, M. J. *Tetrahedron Lett.* **1964**, 1203–1207.

(32) Murov, S. L. *Handbook of Photochemistry*; Marcel-Dekker: New York, 1973.

general[26,29a] and are assignable as the α,β-unsaturated ketones **2a–c** produced as a result of decarbonylation. Comparatively, the absorbance changes (310–700 nm) resulting from 308-nm laser flash excitation of **1d** are very weak (under analogous conditions of laser intensity and ground-state absorbance at 308 nm); this is probably due to the low absorption intensity of the decarbonylation product **6d** at 310–360 nm and/or a low quantum yield of photodecarbonylation. The stabilization of the radical center by aryl substituents at the C-3 position in the course of photoextrusion of CO appears to be important in determining the quantum yield of formation of the decarbonylation products. In our experience, the singlet-mediated photoelimination of CO is the most facile in the case of 3,3-diaryl-substituted 2(3*H*)-furanones.[26,29a]

No short-lived transients, assignable as triplets of **1a–d** (see later), are formed under the direct laser excitation (308 nm); the intersystem crossing yields are negligible (<1%) for these systems in benzene. Also, among **1a–c**, the singlet-mediated bond homolysis at the C-3 position leading to benzyl and furanoxy radicals is nonnegligible only in the case of **1c** (Figure 1B). That the production of furanoxy radical in the case of **1c** is not from the triplet state and also is not a manifestation of sensitization by an impurity triplet is established by the lack of observation of slow formation of the radical. By comparing the end-of-pulse absorbance changes due to furanoxy radicals at 445–460 nm (second absorption band system) with those due to BP triplet in optically matched solutions in benzene, the quantum yields of fast bond cleavage (at the C-3 position) occurring from short-lived photoexcited states (singlets/higher lying triplets) are estimated to be ≤0.03, ≤0.03, and 0.1 for **1a**, **1b**, and **1c**, respectively (in benzene).[29b]

The transient phenomena observed upon 308- or 337.1-nm laser flash photolysis of **1e** are dominated by its triplet with an absorption spectrum (λ_{max}^{T} = 490 nm in benzene) very similar to that of phenanthrene. Some of the results have been described in a previous paper.[27] On the basis of a comparison of end-of-pulse transient absorbances due to **1e** and BP in optically matched benzene solutions (λ_{ex} = 337.1 nm) and the assumption that the maximum triplet–triplet extinction coefficient of **1e** is identical with that of phenanthrene ($\epsilon_{max}^{T} = 1.6 \times 10^4$ M^{-1} cm^{-1} at 493 nm in benzene),[33] we have determined the triplet yield (ϕ_T) of **1e**. The value obtained for ϕ_T in benzene is 0.3. Also, **1e** exhibits a blue fluorescence characterized by a relatively long lifetime (τ_F = 25 ns in benzene, compared to τ_F = 55 ns for phenanthrene in the same solvent). The formation of furanoxy radical **7a** in high yields upon direct laser photolysis of **1f** has been described elsewhere.[28]

The 337.1-nm laser flash excitation of BP in the presence of 20–25 mM **1a–c** in benzene or acetonitrile gives rise to transient processes illustrated by kinetic traces in Figure 2 (with **1c** as a representative example). The observed processes are explainable in terms of the steps in eq 1–6.

$$\mathrm{BP} \xrightarrow{h\nu} {}^1\mathrm{BP}^* \xrightarrow{\mathrm{ISC}} {}^3\mathrm{BP}^* \tag{1}$$

$${}^3\mathrm{BP}^* + \mathbf{1x} \rightarrow \mathrm{BP} + {}^3\mathbf{1x}\ (\mathrm{x} = \mathbf{a}\text{–}\mathbf{d}) \tag{2}$$

$${}^3\mathbf{1x}^* \rightarrow \mathbf{7x} + \mathbf{8} \tag{3}$$

$$\mathbf{7x} + \mathbf{7x} \rightarrow \mathbf{10x} \tag{4}$$

$$\mathbf{7x} + \mathbf{8} \rightarrow \mathbf{1x} \text{ or } \mathbf{9x} \tag{5}$$

$$\mathbf{8} + \mathbf{8} \rightarrow C_6H_5CH_2CH_2C_6H_5 \tag{6}$$

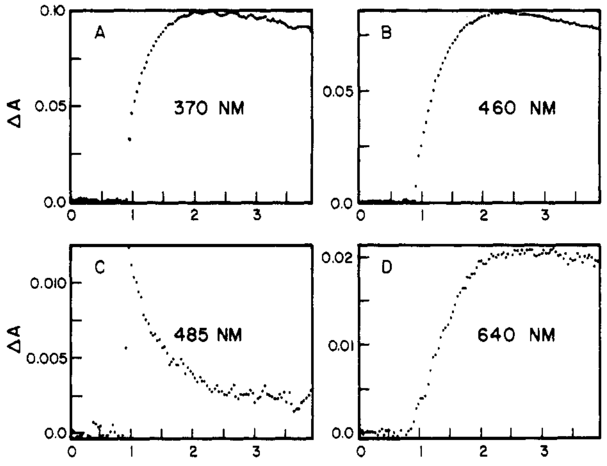

Figure 2. Representative kinetic traces for transient absorptions observed upon 337.1-nm laser flash excitation of 5 mM benzophenone in the presence of 21 mM **1c** in benzene. The monitoring wavelengths are shown in the figures.

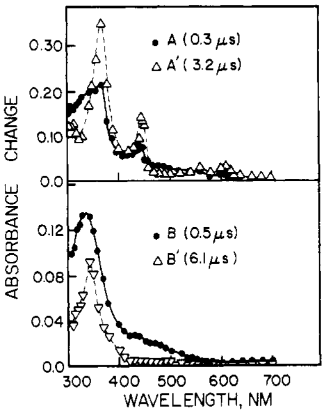

Figure 3. Transient absorption spectra observed upon 337.1-nm laser excitation of 5 mM benzophenone in the presence of (A, A′) 20 mM **1a** and (B, B′) 23 mM **1d** in benzene. The times after laser flash at which the spectra were recorded are shown in the figures.

Note that at the high concentrations we have used for **1a–c** in these experiments, the bimolecular energy-transfer step (eq 2) is fast. The pseudo-first-order rate constants for this step are $\geq 4 \times 10^7$ s^{-1}. The growth processes for transient absorption (Figure 2A,B,D) are observed at or near the absorption maxima of the furanoxy radicals. The absorption spectra of these radicals consist of three-band systems in the spectral region 330–650 nm. Photogenerated by various substrates, the furanoxy radicals have been characterized in an earlier study.[28] The growth processes represent the fragmentation of the triplets of **1a–c** into furanoxy and benzyl radicals (eq 3). Concomitant to the growth processes, we observe the decay of transient absorption at 470–490 nm (Figure 2C); the latter constitutes a spectral window where the absorptions of the triplets of **1a–c** dominate over those of respective furanoxy radicals.

Figure 3 shows the transient absorption spectra observed upon 337.1-nm laser flash excitation of BP in the presence of high concentrations of **1a** and **1d**. The growth and decay processes mentioned above are self-explanatory from the transient spectra in Figure 3A,A′. Note that the kinetic trace at 620 nm (Figure 2C) and the long-wavelength portion of spectrum A in Figure 3 (610–700 nm) are distorted because of underlying contributions of delayed emission from the furanoxy radical. This long-lived emission results from triplet–doublet energy transfer: ${}^3\mathbf{1a}^*$

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

Table I. Kinetic Data Concerning Triplets of 3-Benzyl-2(3*H*)-furanones in Benzene at 295 K

		$10^9 k_q^T$, M^{-1} s^{-1} [b]		
substrt	τ_T, μs[a]	O_2	DMHD	ferrocene
1a	0.52 (0.56)	1.5	0.92	4.4
1b	0.53 (0.62)	1.4	0.97	3.8
1c	0.47 (0.58)	1.7	0.97	4.0
1d	2.3 (3.0)	1.8	0.53	4.0
1e	33[c] (20)[c]	0.6[d]	1.3[d]	3.4

[a] Except for **1e**, the triplet lifetimes were measured with 22–25 mM solutions of 2(3*H*)-furanone substrates under benzophenone sensitization (λ_{ex} = 337.1 nm). For **1e**, the direct excitation (337.1 nm) of ~1 mM solution was used. The data in parentheses are in acetonitrile. [b] ±15%. [c] These lifetimes were measured at very low laser intensities and are longer than τ_T reported in ref 26. [d] Data taken from ref 26.

+ **7a** → **1a** + ^{2}**7a***. The latter phenomenon and emission properties of furanoxy radicals have been described in an earlier report.[27] In the case of **1d**, at the time scale of the decay of its triplet (Figure 3B,B′), we do not observe any growth process in the spectral region 310–700 nm. The residual absorption following the triplet decay shows its maximum at 330 nm (Figure 3B′) and is attributed to the furanoxy radical **7d** derived from **1d**. The residual absorption at 310–350 nm is not due to the rearranged 2(5*H*)-furanone **9d** that could in principle be formed as a result of [1,3]-sigmatropic shift of a 2-benzyl group in the triplet state of **1d**; this is established by the fact that on a longer time scale (~130 μs), the transient absorption at 330 nm is found to undergo substantial decay (that is, the photoproduct in question is not permanent).

The kinetic behaviors of the triplets of **1a–d** have been studied by monitoring them at 470–490 nm. A study of the rate constants for the decay of the triplets of **1a** and **1d** at varying ground state concentrations (5–25 mM) in benzene showed that those were practically independent of the ground-state concentration. The triplet self-quenching rate constants were estimated to be small (≤1 × 10^7 M^{-1} s^{-1}). The triplet lifetime data as well as the rate constants (k_q^T) for the quenching of the triplets by typical triplet quenchers, namely, oxygen, 2,5-dimethyl-2,-hexadiene (DMHD), and ferrocene, are presented in Table I. The fact that the rates of quenching by DMHD are below the limit of diffusion control suggests that the triplet energies of **1a–d** are lower than E_T of DMHD (59 kcal/mol).[32]

Based on the assumption that the triplets of **1a–c** decay entirely by the fragmentation process (eq 3), it was possible to estimate the extinction coefficients of the furanoxy radicals. In these measurements, the transient absorbances (ΔOD_{BP}^T) due to BP triplet in the absence of a quencher were compared with the maximum absorbances (ΔOD_F^R) observed for furanoxy radicals at the completion of their formation in BP solutions containing 25–30 mM **1a–c**. Equation 7 was used for calculation of the extinction coefficients (ϵ_F^R) of the radicals; those of BP triplet in

$$\epsilon_F^R = \epsilon_{BP}^T \frac{\Delta OD_F^R}{\Delta OD_{BP}^T} \qquad (7)$$

benzene and acetonitrile were taken to be 7.6 × 10^3 and 6.5 × 10^3 M^{-1} cm^{-1}, respectively.[33,34] The absorption spectral data of furanoxy radicals are compiled in Table II. Note that the ϵ_F^R values in benzene and acetonitrile (Table II) are slightly different from those in 1:2 benzene/di-*tert*-butyl peroxide reported earlier.[28] The difference is in part due to experimental errors and may in part be related to solvent effect.

Table II. Spectral and Kinetic Data Concerning Furanoxy Radicals Derived from 1a–c by Benzophenone Triplet Sensitization at 295 K

	benzene		acetonitrile	
substrt	λ_{max}, nm[a]	$10^3\epsilon_{max}$, M^{-1} cm^{-1} [b]	λ_{max}, nm[a]	$10^3\epsilon_{max}$, M^{-1} cm^{-1} [b]
1a	370	21	365	15
	445	8.7	445	5.6
	610	1.4	610	1.1
1b	370	20	370	14
	450	11	450	6.5
	620	1.9	620	1.4
1c	370	17	370	14
	460	15	460	8.6
	640	3.5	635	2.9

[a] ±5 nm. [b] ±20%; since the calculation of the ε values was based on the assumption that the decay of the triplets of **1a–c** is entirely controlled by the fragmentation process (eq 3), they actually represent the lower limits.

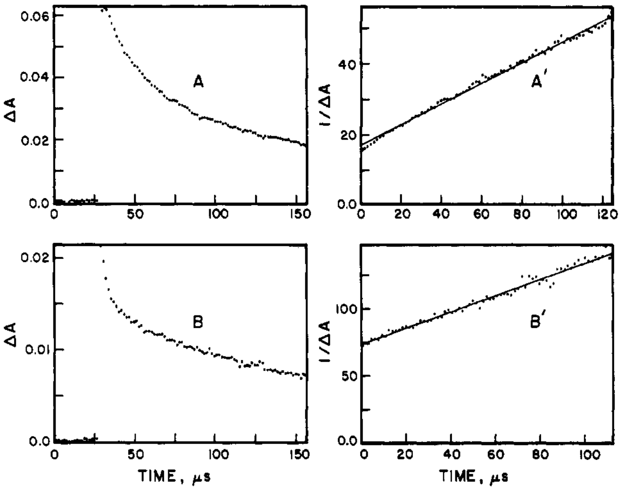

Figure 4. (A, B) Kinetic traces for decay of furanoxy radicals and (A′, B′) plots of the absorbance data into second-order equal-concentration kinetics. The traces were obtained by 337.1-nm laser flash excitation of 5 mM benzophenone in the presence of (A, A′) 20 mM **1a** and (B, B′) 23 mM **1d** in benzene. The initial fast-decaying transient absorption in the case of **1d** in B is due to the triplet of **1d**. The monitoring wavelengths are 370 and 330 nm for A and B, respectively.

The decay of furanoxy radicals observed on a long time scale (~130 μs) gives the appearance of second-order kinetics. However, the fitting of the decay profiles in the case of **1a–c** into second-order equal-concentration kinetics was not satisfactory (for example, see Figure 4A,A′); the experimental points in the initial parts of the decay profiles were always higher than those obtained from best-fit calculated curves. This is understandable in view of the coupled processes, eq 4–6, being responsible for the disappearance of the radicals. That, at least, the processes in eq 4 and 5 are important is suggested by the isolation of products **10a–c** and **9a–c** from the photolysates of sensitized irradiation (vide supra). On the other hand, in the case of **1d**, the decay of the furanoxy radical is slower and gives relatively better fits into second-order equal-concentration kinetics (Figure 4B,B′). This may be a reflection of the fact that, among the processes in eq 4–6, the process in eq 5 represents the predominant pathway for the decay of the radicals. This is supported by the fact that the rearranged 2(5*H*)-furanone **9d** is the only major

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(34) Bensasson, R.; Gramain, J.-C. *J. Chem. Soc., Faraday Trans. 1* **1980**, *76*, 1801–1810.

(35) Haddadin, M. J.; Agha, B. J.; Tabri, R. F. *J. Org. Chem.* **1979**, *44*, 494–497.

(36) Sullivan, W. W.; Ullmann, D.; Shechter, H. *Tetrahedron Lett.* **1969**, 457–461.

photoproduct in the course of sensitized photolysis of **1d** (vide supra). On the basis of the fit of Figure 4B′, k/ϵ for reaction 5 is calculated as 1.2×10^5 cm s^{-1} (at 330 nm in benzene).

The short triplet lifetimes of the 2(3*H*)-furanones reflect their reactive nature. In a parallel study[29a] on 3,3,5-triaryl-substituted 2(3*H*)-furanones we have observed triplet lifetimes mostly in the vicinity of 1 μs. These molecules undergo intramolecular 3,4-aryl group migration in the triplet state, producing rearranged 3,4,5-triaryl-substituted 2(5*H*)-furanones. For the 3-benzyl-substituted 2(3*H*)-furanones **1a–c** under consideration, the triplet lifetimes are even shorter and are associated with the facile bond cleavages followed by efficient separation into a pair of solvated radicals. The latter process is aided by the fact that the radical recombination in the geminate radical pair is spin-forbidden because of the triplet configuration of the pair; this also is probably the major reason why the bond cleavage is inefficient from the singlet state (i.e., upon direct excitation). Note that the triplet lifetimes of **1d** and **1e** are significantly longer than those of **1a–c** (Table I), suggesting the less facile nature of the bond cleavage in these two cases. For **1d**, this is explainable in terms of greater strength of the bond to be cleaved, that is, the reduced stability of the resultant furanoxy radical (because of the absence of the 3-phenyl group that contributes to the delocalization of the unpaired electron). For **1e**, the excitation energy is spread in the extended π-system of the phenanthrene moiety and is, on the average, relatively distant from the vulnerable bond. This spatial factor may be responsible for the inefficiency of bond cleavage in the triplet of **1e**.

Experimental Section

All melting points are uncorrected and were determined in a Mel-Temp melting point apparatus. The IR spectra were recorded on Perkin-Elmer Model 377 and Model 580 infrared spectrophotometers. The electronic spectra were obtained on a Beckman DB or Cary 17D spectrophotometer. The ^{1}H NMR traces were recorded on either a Varian A-60 or an EM-390 spectrometer, using tetramethylsilane as internal standard. For mass spectra, use was made of single-focusing Hitachi RMU-6E or a Varian Mat CH7 mass spectrometer at 70 eV. Irradiations were carried out in a Srinivasan-Griffin Rayonet photochemical reactor (RPR 3000 or 3500 Å) or with a Hanovia 450-W medium-pressure mercury lamp in a quartz-jacketed immersion well.

Starting Materials. 2(3*H*)-Furanones **1a**, mp 148–149 °C,[28] **1b**, mp 164–165 °C,[28] **1c**, mp 138–139 °C,[28] **1e**, mp 225–226 °C,[26] and **1f**, mp 185–186 °C,[37] were prepared by reported procedures. Solvents such as benzene and methanol used for steady-state irradiation experiments were purified by standard procedures. Petroleum ether used was the fraction with bp 60–80 °C.

Preparation of 1d. To a suspension of sodium hydride (0.24 g, 0.01 mol) in anhydrous tetrahydrofuran (50 mL) was added 5-phenyl-2(3*H*)-furanone[38] (1.5 g, 0.01 mol) and warmed on a water bath at 55–60 °C for 0.5 h. The mixtue was then cooled to 5 °C and benzyl benzenesulfonate (2.48 g, 0.01 mol) was added and the mixture stirred at 5–10 °C for 12 h. The inorganic salt that separated out was filtered off and the solvent removed under vacuum to give a residue, which was crystallized from methanol to give 1.03 g (30%) of **1d**, mp 176–177 °C: IR ν_{max} (KBr) 3100, 3070, 3050, 3020, 2920 (CH), 1770 (C=O), 1650, and 1600 (C=C) cm^{-1}; UV λ_{max} (methanol) 262 nm (ϵ 14 100), 267 (sh, 13 600); ^{1}H NMR (CDCl$_3$) δ 3.1 (4 H, q, J = 14 Hz; CH$_2$ inequivalent due to restricted rotation), 5.7 (1 H, s, vinylic), 7.19 (15 H, m, Ar).

Anal. Calcd for $C_{24}H_{20}O_2$: C, 84.71; H, 5.88. Found: C, 84.35; H, 5.80.

Irradiation of 2(3*H*)-furanones 1a–f. A general procedure for direct irradiation was to photolyze 0.5–1.0 mM solutions of the furanones in benzene or methanol with either a 3000-Å light source or a Hanovia 450-W medium-pressure mercury lamp. In sensitization experiments, ~5 mM solutions of **1a–d** in benzene containing acetophenone (3 mM) were irradiated in Pyrex vessels using a 3500-Å light source. In each case, following the removal of the solvent under vacuum, the residual solid was chromatographed over silica gel and eluted with different solvents to give the products. The latter were purified by recrystallization from suitable solvents.

Irradiation of 1a. A benzene solution of **1a** (350 mg, 1.07 mmol) was irradiated for 0.5 h and worked up to give 25 mg (8%) of **3a**, mp 92–93 °C (mixture melting point)[35] (elution with petroleum ether), 70 mg (20%) of **6a**, mp 132–133 °C (elution with a 2:3 mixture of benzene and petroleum ether), and 121 mg (34%) of the unchanged starting material **1a**, mp 148–149 °C (mixture melting point).

6a: IR ν_{max} (KBr) 3080, 3050, 3020 (CH), 1684 (C=O), 1595, and 1580 (C=C) cm^{-1}; UV λ_{max} (methanol) 223 nm (ϵ 22 100), 244 (23 100); ^{1}H NMR (CDCl$_3$) δ 4.35 (2 H, s, methylene, 7.05 (1 H, s, vinylic), 7.55 (15 H, m, Ar); mass spectrum, m/e (relative intensity) 298 (M$^+$, 20), 193 (M$^+$ − 105, 5), 179 (M$^+$ − 119, 1), 178 (M$^+$ − 120, 7), and other peaks.

Anal. Calcd for $C_{22}H_{18}O$: C, 88.59; H, 6.04. Found: C, 88.86; H, 5.92.

In repeat run, a methanol solution of **1a** (250 mg, 0.77 mmol) was irradiated for 0.5 h and worked up to give 20 mg (9%) of **3a**, 60 mg (26%) and **6a**, and 94 mg (37%) of unchanged starting material.

In another experiment, a benzene solution of **1a** (200 mg, 0.16 mmol) containing acetophenone (3 mM solution) was irradiated for 3 h and worked up to give 70 mg (35%) of **9a**, mp 163–164 °C (elution with a mixture (1:1) of benzene and petroleum ether, 40 mg (27%) of **10a**, mp 285–288 °C (mixture melting point)[22] (obtained by triturating the residue by methanol followed by filtration), and 50 mg (25%e of the unchanged starting material, mp 148–149 °C (mixture melting point).

9a: IR ν_{max} (KBr) 3080, 3060, 3020 (CH), 1740 (C=O), 1600, and 1500 (C=C) cm^{-1}; UV λ_{max} (methanol) 259 nm (ϵ 21 200), 264 (21 000); ^{1}H NMR (CDCl$_3$) δ 3.4 (2 H, s, methylene), 7.35 (16 H, m, Ar and vinylic).

Anal. Calcd for $C_{23}H_{18}O_2$: C, 84.66; H, 5.52. Found: C, 85.02; h, 5.45.

Irradiation of 1b. A benzene solution of **1b** (350 mg, 1.05 mmol) was irradiated for 0.5 h and worked up to give 20 mg (6%) of **3b**, mp 126–127 °C (elution with petroleum ether), 101 mg (31%) of **6b**, mp 64–65 °C (elution with a mixture (2:3) of benzene and petroleum ether), and 192 mg (54%) of the unchanged starting material, mp 164–165 °C (mixture melting point).

3b: IR ν_{max} (KBr) 3040, 3020, 3000, 2910, (CH), 1580 (C=C), and 1140 (C–O) cm^{-1}; UV λ_{max} (methanol) 240 nm (ϵ 12 400), and 266 (17 600); ^{1}H NMR (CDCl$_3$ δ 2.4 (3 H, s, methyl), 6.75 (1 H., s, vinylic), 7.45 (14 H, m, Ar).

Anal. Calcd for $C_{23}H_{18}O$: C, 89.03; H, 5.81. Found: C, 88.72; H, 5.50.

6b: IR ν_{max} (KBr) 3040, 3020, 2920 (CH), 1680 (C=O), 1595, and 1570 (C=C) cm^{-1}; UV λ_{max} (methanol) 220 nm (ϵ 21 700), 250 (21 700); ^{1}H NMR (CDCl$_3$) δ 2.4 (3 H, s, methyl), 4.53 (2 H, s, methylene), 6.66 (1 H, s, vinylic), 7.71 (14 H, m, Ar).

Anal. Calcd for $C_{23}H_{20}O$: C, 88.46; H, 6.41. Found: C, 88.06; H, 6.23.

In a repeat run, a solution of **1b** (200 mg, 0.6 mmol) in methanol was irradiated for 0.5 h and worked up to give 24 mg (13%) of **3b**, 40 mg (21%) of **6b**, and 80 mg (40%) of the unchanged starting material.

In another experiment, a solution of **1b** (400 mg, 1.17 mmol) in benzene containing acetophenone was irradiated for 3 h and worked up to give 200 mg (50%) of **9b**, mp 140–141 °C (elution with a mixture (1:1) of benzene and petroleum ether), 20 mg (7%) of **10b**, mp 258–260 °C (obtained by filtration), and 10 mg (25%) of the unchanged starting material, mp 164–165 °,c (mixture melting point).

9b: IR ν_{max} (KBr) 3090, 3020, 2920 (CH), 1745 (C=O), 1500, and 1490 (C=C) cm^{-1}; UV λ_{max} (methanol) 264 nm (ϵ 9200), 270 (9400); ^{1}H NMR (CDCl$_3$) δ 2.53 (3 H, s, methyl), 3.6 (2 H, s,

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(37) Wasserman, H. H.; Pavia, D. L. *J. Chem. Soc., Chem. Commun.* **1970**, 1459–1460.

(38) Miller, G. A.; Heindel, N. D.; Minatelli, J. A. *J. Heterocycl. Chem.* **1981**, *18*, 1253–1254.

methylene), 7.48 (15 H, m, Ar and vinylic).

Anal. Calcd for $C_{24}H_{20}O_2$: C, 84.71; H, 5.88. Found: C, 84.30; H, 5.42.

Irradiation of 1c. A benzene solution of **1c** (200 mg, 0.56 mmol) was irradiated for 0.5 h and worked up to give 15 mg (8%) of **3c**, mp 120–121 °C (elution with petroleum ether), 47 mg (25%) of **6c**, mp 112–113 °C (elution with a mixture (2:3) of benzene and petroleum ether), and 100 mg (50%) of the unchanged starting material, mp 138–139 °C (mixture melting point).

3c: IR ν_{max} (KBr) 3100, 3040, 2950 (CH), 1600 (C=C), 1250, and 1020 (C–O) cm^{-1}; UV λ_{max} (methanol) 246 nm (ϵ 11 600), 270 (22 400); ^{1}H NMR (CDCl$_3$) δ 3.9 (3 H, s, methoxy), 6.83 (1 H, s, vinylic), 7.5 (14 H, m, Ar).

Anal. Calcd for $C_{23}H_{18}O_2$: C, 84.66; H, 5.52. Found: C, 84.50; H, 5.28.

6c: IR ν_{max} (KBr) 3080, 3020, 2950, 2900 (CH), 1680 (C=O), 1605, and 1595 (C=C) cm^{-1}; UV λ_{max} (methanol) 245 nm (ϵ 54 000), 277 (53 000); ^{1}H NMR (CDCl$_3$) δ 3.75 (3 H, s, methoxy), 4.3 (2 H, s, methylene), 6.7 (1 H, s, vinylic, 7.5 (14 H, m, Ar); mass spectrum, *m/e* (relative intensity) 328 (M$^+$, 24), 223 (M$^+$ – 105, 6), 208 (M$^+$ – 120, 2), and other peaks.

Anal. Calcd for $C_{23}H_{20}O_2$: C, 84.14; H, 6.1. Found: C, 84.47; H, 5.82.

In a repeat run, a methanol solution of **1c** (200 mg, 0.56 mmol) was irradiated for 0.5 h and worked up to yield 20 mg (11%) of **3c**, 44 mg (24%) of **6c**, and 100 mg (50%) of the unchanged starting material.

In another experiment, a benzene solution of **1c** (400 mg, 1.12 mmol) containing acetophenone was irradiated for 3 h and worked up to give 190 mg (47%) of **9c**, mp 153–154 °C (elution with a mixture (1:1) of benzene and petroleum ether), 20 mg (6%) of **10c**, mp 230–233 °C (obtained by filtration), and 100 mg (25%) of the unchanged starting material, mp 138–139 °C (mixture melting point).

9c: IR ν_{max} (KBr) 3080, 3020, 2950, 2830 (CH), 1740 (C=O), 1605, and 1510 (C=C) cm^{-1}; UV λ_{max} (methanol) 281 nm (ϵ 10 500), 296 (sh, 8800); ^{1}H NMR (CDCl$_3$) δ 3.35 (2 H, s, methylene), 3.75 (3 H, s, methoxy), 7.22 (15 H, m, Ar and vinylic).

Anal. Calcd for $C_{24}H_{20}O_3$: C, 80.89; H, 5.62. Found: C, 80.68, H, 5.45.

In yet another run, a solution of **1c** (800 mg, 2.3 mmol) in benzene (25 mL) containing acetophenone (120 mg, 1 mmol) was irradiated (RPR 3500 Å) for 14 h. The ^{1}H NMR of the crude photolysate indicated the presence of bibenzyl. The photolyzed mixture was subsequently worked up as in the earlier cases to give 15 mg (7%) of bibenzyl (confirmed by ^{1}H NMR (CDCl$_3$) δ 2.9 (4 H, s, methylene), 7.2 (10 H, br s, Ar)) (elution with petroleum ether), 485 mg (60%) of **9c**, mp 153–154 °C (mixture melting point) (elution with a mixture (1:1) of benzene and petroleum ether), 73 mg (12%) of **10c**, mp 220–223 °C (mixture melting point), and 141 mg (18%) of the unchanged starting material, mp 138–139 °C (mixture melting point).

Irradiation of 1d. A benzene solution of **1d** (340 mg, 1 mmol) was irradiated for 4 h and worked up to yield 250 mg (80%) of **6d**, mp ca. 20 °C (elution with a mixture (1:4) of benzene and petroleum ether) and 40 mg (12%) of unchanged starting material, mp 175–176 °C (mixture melting point).

6d: IR ν_{max} (neat) 3050, 3020, 2910, 2480 (CH), 1670 (C=O), 1610, and 1595 (C=C) cm^{-1}; UV λ_{max} (methanol) 254 nm (ϵ 14 000), 262 (sh, 13 300); ^{1}H NMR (CDCl)$_3$ δ 3.43 (2 H, s, methylene), 3.97 (2 H, s, methylene), 6.73 (1 H, s, vinylic), 7.5 (15 H, m, Ar); mass spectrum, *m/e* (relative intensity) 312 (M$^+$, 27), 221 (M$^+$ – 91, 75), 207 (M$^+$ – 120, 3), 105 ($C_6H_5CO^+$, 100), 91 ($C_6H_5CH_2^+$, 65), and other peaks.

Anal. Calcd for $C_{23}H_{20}O$: C, 88.46; H, 6.41. Found: C, 88.85; H, 6.34.

In a repeat experiment, a methanol solution of **1d** (340 mg, 1 mmol) was irradiated for 4 h and worked up to give 260 mg (83%) of **6d** and 50 mg (14%) of the unchanged starting material.

In another run, a benzene solution of **1d** (340 mg, 1 mmol) containing acetophenone was irradiated for 3 h and worked up to give 90 mg (23%) of **9d**, mp 135–136 °C (elution with a mixture (3:2) of benzene and petroleum ether) and 200 mg (58%) of the unchanged starting material, mp 175–176 °C (mixture melting point).

9d: IR ν_{max} (KBr) 3090, 3050, 3020, 2910 (CH), 1740 (C=O), and 1600 (C=C) cm^{-1}; UV λ_{max} (methanol) 258 nm (ϵ 2100), 263 (sh, 1700); ^{1}H NMR (CDCl$_3$) δ 3.28 (2 H, q, *J* = 14 Hz, C-5 methylene) 3.35 (2 H, s, C-3 methylene), 7.15 (16 H, m, Ar and vinylic).

Anal. Calcd for $C_{24}H_{20}O_2$: C, 84.71; H, 5.88. Found: C, 84.31, H, 5.57.

Irradiation of 1e. A benzene solution of **1e** (100 mg, 0.25 mmol) was irradiated for 10 h and worked up to give 15 mg (15%) of **3e**, mp 192–193 °C (lit.[36] mp 193–194 °C) (elution with a mixture (1:4) of benzene and petroleum ether) and 45 mg (45%) of the unchanged starting material, mp 225–225 °C (mixture melting point).

In a repeat run, a methanol solution of **1e** (100 mg, 0.25 mmol) was irradiated for 10 h and worked up to give 20 mg (21%) of the unchanged starting material.

Irradiation of 1f. A benzene solution of **1f** (340 mg, 1 mmol) was irradiated for 3 h and worked up to give 170 mg (72%) of **10a**, mp 285–288 °C (mixture melting point).

In a repeat run, a methanol solution of **1f** (200 mg, 0.59 mmol) was irradiated for 3 h and worked up to give 105 mg (75%) of **10a**.

Thermolysis of 2(3*H*)-Furanones 1a–d. The general procedure for thermolysis experiments was to heat 100 mg of the furanones in sealed tubes at 250 °C for 2 h. In each case, the residue obtained was extracted with dichloromethane and crystallized from ethanol to obtain the products. The products and their yields from **1a**, **1b**, **1c**, and **1d** were the following, respectively: **9a** (60%, mp 163–164 °C, (mixture melting point)), **9b** (80%, mp 140–141 °C (mixture melting point)), **9c** (75%, mp 153–154 °C (mixture melting point)), and **9d** (70%, mp 135–136 °C (mixture melting point)).

Laser Flash Photolysis. The laser pulse excitation was carried out in a front-face geometry with 308-nm laser pulses (20 ns, ≤100 mJ) from a Lambda-Physik EMG MSC 101 excimer system or with 337.1 nm laser pulses (8 ns, 2–3 mJ) from a Molectron UV-400 nitrogen laser source. The kinetic spectrophotometer and the data collection system are described elsewhere.[39,40] Unless a study of the effect of oxygen was intended, the experiments were performed with solutions deoxygenated by saturation with high-purity argon.

Registry No. **1a**, 97861-38-6; **1b**, 97861-39-7; **1c**, 97861-40-0; **1d**, 7404-47-9; **1e**, 92545-49-8; **1f**, 31994-73-7; **3b**, 110851-33-7; **3c**, 36846-09-0; **3e**, 22725-49-1; **6a**, 110851-31-5; **6b**, 110851-34-8; **6c**, 110851-37-1; **6d**, 110851-40-6; **9a**, 110851-32-6; **9b**, 110851-35-9; **9c**, 110851-38-2; **9d**, 110851-41-7; **10a**, 5369-54-0; **10b**, 110851-36-0; **10c**, 110851-39-3.

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(39) Das, P. K.; Encinas, M. V.; Small, R. D., Jr.; Scaiano, J. C. *J. Am. Chem. Soc.* **1979**, *101*, 6965–6970 and earlier references cited therein.

(40) Nagarajan, V.; Fessenden, R. W. *J. Phys. Chem.* **1985**, *89*, 2330–2335.