

($B = 5.0 \text{ \AA}^2$). In the final cycles of least-squares refinements the structure converged (max shift 0.030) using 2080 reflections ($I \geq 2\sigma(I)$) on 304 variables. Variables included the overall scale factor, positional parameters for all atoms, and anisotropic thermal parameters for all non-hydrogen atoms. Convergence was achieved with final R values of $R_1 = 0.036$, $R_2 = 0.046$, and an ESD of 1.563 using a non Poisson type distribution²³ with a weighting factor of 0.04. A final difference Fourier map showed no peaks greater than 0.27 e \AA^{-3} .

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Registry No. 2, 21879-81-2; (\pm)-2, 97467-36-2; 4b, 73912-36-4; 4c, 52062-24-5; 6, 14918-66-2; 10, 67402-67-9; 18, 13379-22-1; 19, 97467-30-6; 20a, 97485-97-7; 20b, 97485-99-9; 20b (regioisomer), 97486-00-5; 20c, 97467-33-9; (\pm)-21, 97467-32-8; (\pm)-21 (7-TMS ether), 97485-98-8; 22, 67402-63-5; 23, 67402-64-6; (\pm)-24, 97467-37-3; 28, 97467-34-0; 28 (regioisomer), 97467-38-4; 30, 97467-31-7; 31, 67402-70-4; 31 (regioisomer), 97467-39-5; (\pm)-32, 97467-35-1; Ph_2CCl_2 , 2051-90-3.

Supplementary Material Available: Tables of positional parameters, bond lengths, bond angles, and U values for the structure determination of (\pm)-24 (5 pages). Ordering information is given on any current masthead page. Tables of calculated and observed structure factors (F_o and F_c) are available from the authors.

(23) $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$, $R_2 = [\sum \omega (|F_o| - |F_c|)^2 / \sum \omega F_o^{21/2}]^{1/2}$, $\omega = 1/(\sigma(F_o))^2$, $\sigma(F_o) = \sigma(F_o^2) / 2F_o$, $\sigma(F_o^2) = [(\sigma(I_{\text{raw}}))^2 + (0.04F_o^2)^2]^{1/2}$; ESD is the estimated standard deviation of an observation of unit weight.

Photoinduced Electron-Transfer Reactions of 2(3H)-Furanones and Bis(benzofuranones). Spectral and Kinetic Behavior of Radicals and Radical Cations¹

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The spectral and kinetic behaviors of radical cations produced under efficient electron-transfer quenching of 1,4-dicyanonaphthalene or 9,10-dicyanoanthracene singlet by a number of 2(3H)-furanones and bis(benzofuranones) have been examined by nanosecond laser flash photolysis (337.1 and 425 nm). The efficiencies of net electron transfer in the course of quenching processes are moderately high (0.2–0.6) in acetonitrile. The radical cations from bis(benzofuranones) and several 2(3H)-furanones containing a benzyl group at the 3-position undergo fragmentation to benzofuranoxyl and furanoxyl radicals (+ benzyl or benzofuranoyl carbocations) with rate constants of $0.3\text{--}6 \times 10^6 \text{ s}^{-1}$. The long-lived furanoxyl radicals, independently generated via hydrogen abstraction by *tert*-butoxy radicals from 2(5H)-furanones and 3-phenyl-2(3H)-benzofuranone, as well as via direct photolysis of 3-benzoyl-3,5-diphenyl-2(3H)-furanone, are characterized by sharply structured absorption spectra and relatively slow second-order decay kinetics ($6\text{--}8 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$ in 1:2 benzene-*di-tert*-butyl peroxide, v/v).

Oftentimes, organic photoreactions leading to isomerization,³ rearrangement/fragmentation,⁴ small-molecule extrusion,⁵ etc. occur as effectively under electron-transfer (e.t.) photosensitization as under direct irradiation. Characterization of the intermediates, namely, exciplexes, ion pairs, and radical ions, involved in phototransforma-

tions under e.t. sensitization, is critically important for understanding the related photochemical reaction mechanisms. In some cases, the radical ions undergo⁶ cleavage along a weak bond (intramolecular e.t.) giving ions and radicals; the latter then become the active species that undergo addition/disproportionation reactions, form peroxy radicals with oxygen, or initiate polymerization.

In a recent paper,⁷ we have reported on the photochemistry of a number of 2(3H)-furanones and bis(benzofuranones) based on steady-state irradiation, product analysis, and laser flash photolysis. The two major pathways⁷ for photoreactions of 2(3H)-furanones are singlet-mediated decarbonylation to α,β -unsaturated carbonyl compounds and cyclization leading to 4a,4b-dihydro-

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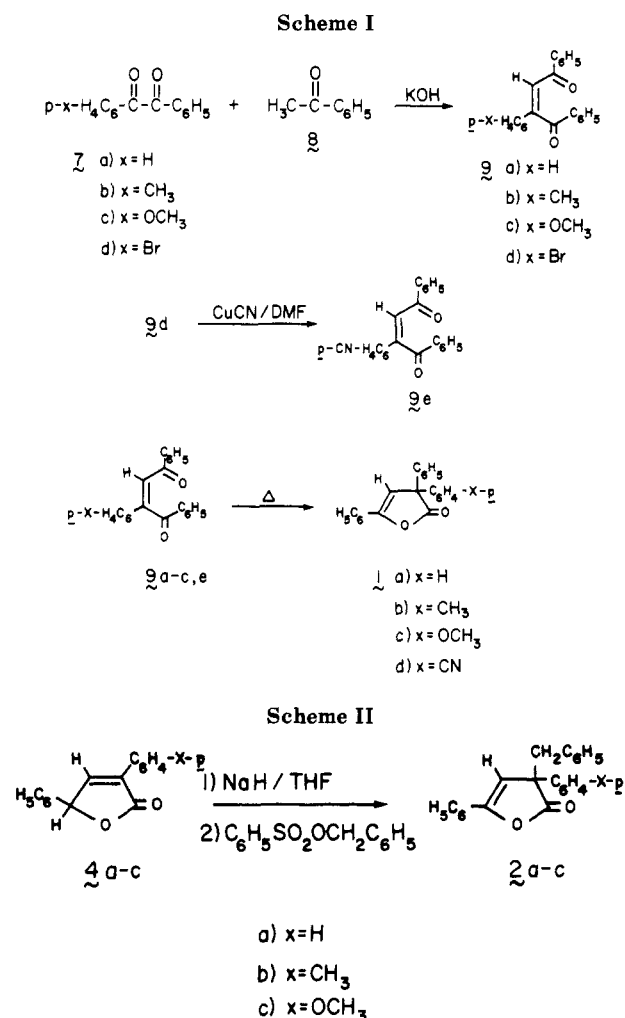
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phenanthrenes. The bis(benzofuranones) give⁷ photo-products explainable in terms of facile homolytic dissociation of these molecules into a pair of benzofuranoxy radicals that act as the primary intermediate. We have now examined the behavior of several of these 2(3*H*)-furanones and bis(benzofuranones) (listed in Chart I) under e.t. photosensitization by cyanoaromatics, based on nanosecond laser flash photolysis and steady-state fluorescence quenching. The preparation of some of these 2(3*H*)-furanones and bis(benzofuranones) was reported earlier,⁷ whereas the others were prepared as per pathways shown in Schemes I and II. 1,4-Dicyanonaphthalene (DCN) and 9,10-dicyanoanthracene (DCA) have been used as the sensitizers (singlet excited-state acceptors). In addition to fluorescence quenching rate constants and quantum efficiencies of radical ion formation, we are presenting results, based on kinetic spectrophotometry, that establish the fragmentation of radical cations from some of the substrates to furanoxo radicals and carbocations on a nanosecond time scale. For the purpose of identification, the furanoxo radicals have also been produced by hydrogen abstraction from several appropriate substrates (4a-c and 6) by photogenerated *tert*-butoxy radical and by direct photolysis of 3-benzoyl-3,5-diphenyl-2(3*H*)-furanone (3, Chart I).

Results

(a) Steady-State Fluorescence Quenching. In acetonitrile, the substrates under study quench the fluorescence of DCN and DCA to variable degrees. The Stern-Volmer quenching constants (K_{SV}^F) were obtained from

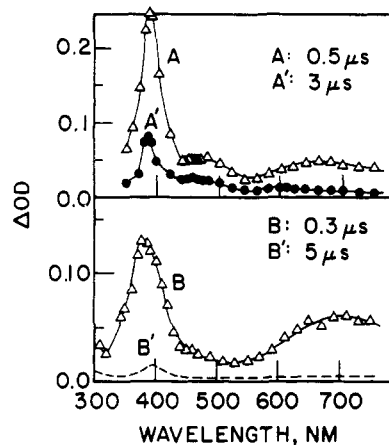
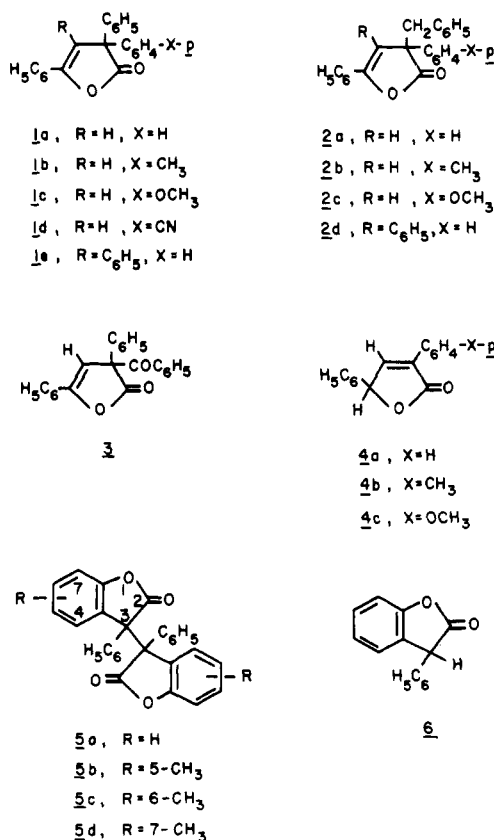


Figure 1. Transient absorption spectra observed upon 337.1-nm laser photolysis of (A, A') 0.70 mM DCN in the presence of 12 mM **1b** in deoxygenated acetonitrile and (B, B') 0.40 mM DCN in the presence of 28 mM **1b** in air-saturated acetonitrile. The spectra correspond to (A) 0.5, (A') 3, (B) 0.3, and (B') 5 μ s following the laser flash.

Chart I



linear plots based on: $I_o^F/I^F = 1 + K_{SV}^F[Q]$, where I_o^F and I^F are steady-state fluorescence intensities of the sensitizer in the absence and in the presence of a quencher (Q), respectively. The fluorescence intensities were monitored at or near the wavelength maxima (380 nm for DCN and 438 nm for DCA). Table I contains the K_{SV}^F data and the related quenching rate constants (k_q^{ss} , calculated from $K_{SV}^F = k_q^{ss}\tau^F$ where τ^F is the fluorescence lifetime of the sensitizer). Laser flash photolysis experiments were confined to the substrates with $k_q^{ss} \geq 5 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ so that DCN (or DCA) singlet quenching were more than 20% at the maximum substrate concentration (50 mM) used. No experiment was feasible with DCN as the photosensitizer for substrates **1d** and **1e** because of strong overlap of their

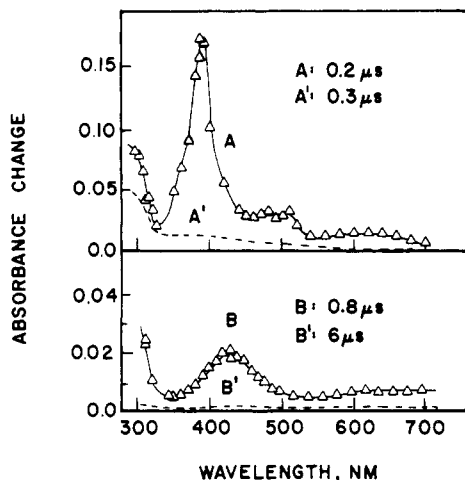


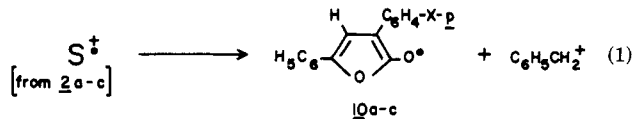
Figure 2. Transient absorption spectra observed upon 337.1-nm laser flash photolysis of 0.5 mM DCN in the presence of (A) 0.07 M styrene in deoxygenated acetonitrile, (A') 0.07 M styrene in air-saturated acetonitrile, and (B, B') 32 mM **1c** in air-saturated acetonitrile. The spectra were taken at (A) 0.2, (A') 0.3, (B) 0.8, and (B') 6 μ s following the laser flash.

ground-state absorption with that of DCN.

(b) Transient Absorption Spectra of Radicals and Radical Ions. The transient absorption phenomena observed upon 337.1 nm laser flash photolysis of DCN in the presence of **1a**, **1b**, and **1d** at 15–50 mM are similar to one another. These are exemplified in Figure 1 with **1b** as the substrate. Under deoxygenated conditions, both DCN radical anion⁸ (DCN^{-•}) and substrate-derived radical cation (S^{+•}) contribute to the absorption maximum at 385–390 nm (Figure 1, parts A and A'), while the broad absorption at longer wavelengths (550–750 nm) is primarily due to S^{+•}. The absorption spectrum of the latter is better resolved upon air saturation (Figure 1, parts B and B') when both DCN^{-•} and ³DCN* become short-lived ($\tau = 50$ and 400 ns, respectively)⁸ owing to oxygen quenching. For comparison, the transient absorption spectra of DCN radical anion and styrene radical cation formed as a result of DCN singlet quenching by styrene in acetonitrile are presented in Figure 2, parts A and A'.

The absorption spectra of the radical cation from 2-(3H)-furanone **1c** obtained via ¹DCN* sensitization in aerated acetonitrile is shown in Figure 2, parts B and B'. The absorption maximum (430 nm) is notably red-shifted relative to those in the cases of **1a,b** and **1d** and the band system at long wavelengths (550–700 nm) is comparatively weak. In fact, the 430-nm band system is reminiscent of the absorption spectrum of 4-methoxytoluene radical cation, observed under similar conditions.

The transient processes observed with 2-(3H)-furanones **2a–c**, each containing the benzyl group at the 3-position (Chart I) show that their radical cations undergo fragmentation on a nanosecond to microsecond time scale to the corresponding furanoxyl radical and benzyl carbonium ion (eq 1). As illustrated in Figure 3 with **2a** as the sub-



strate, for both **2a** and **2b** growths of transient absorption are noticed at 350–380 nm and 400–450 nm; these are concomitant with decay processes seen at 600–750 nm.

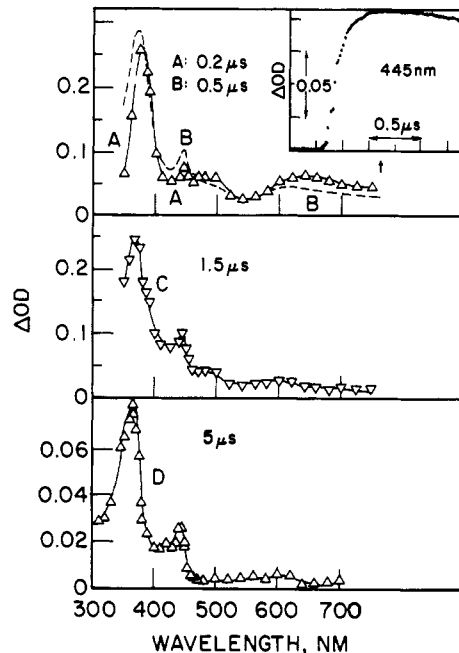


Figure 3. Transient absorption spectra observed upon 337.1-nm laser flash photolysis of (A, B, C) 0.70 mM DCN in the presence of 15 mM **2a** in deoxygenated acetonitrile and (D) 0.50 mM DCN in the presence of 35 mM **2a** in air-saturated acetonitrile. The times, following laser flash, at which the spectra were taken are (A) 0.2, (B) 0.5, (C) 1.5, and (D) 5 μ s. The inset shows the growth of transient absorption at 445 nm in the experiment in which spectra A, B, and C were taken.

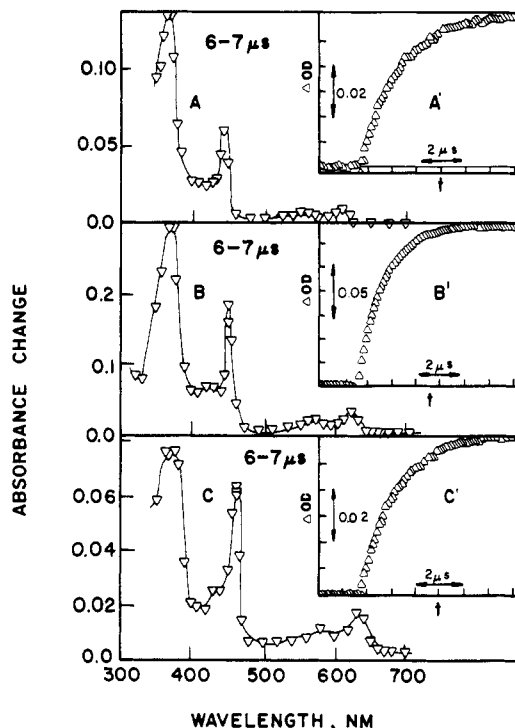


Figure 4. Transient absorption spectra due to furanoxyl radicals, observed at 6–7 μ s following 337.1-nm laser flash photolysis of 1:2 benzene-*di-tert*-butyl peroxide (v/v) containing 25–30 mM of (A) **4a**, (B) **4b**, and (C) **4c**. The insets show kinetic traces for growths of transient absorption at 445–460 nm in respective cases.

That the structured absorption spectra (see Figure 3, part D) at ≤ 5 μ s following the laser flash photolysis of DCN in the presence of **2a–c** in aerated acetonitrile are due to furanoxyl radicals is established by generating the latter via hydrogen abstraction from 2-(5H)-furanones (**4a–c**) by *tert*-butoxy radical. Laser photolysis⁹ (337.1 nm) of di-

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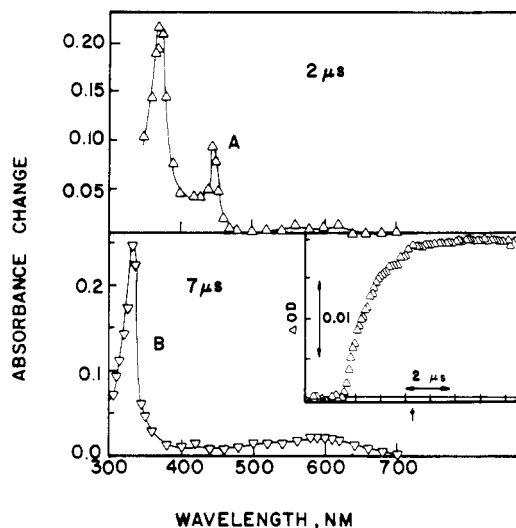
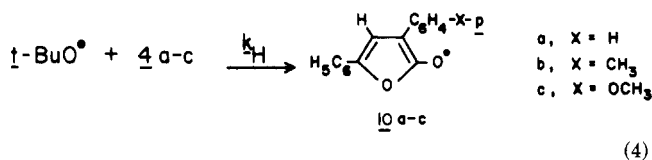
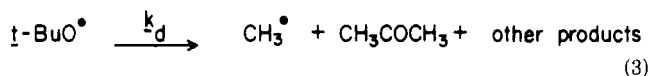
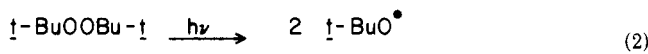


Figure 5. Transient absorption spectra observed upon 337.1-nm laser flash photolysis of (A) **3** in deoxygenated benzene (at 2 μ s after laser flash) and (B) 1:2 benzene-di-*tert*-butyl peroxide (v/v) containing 50 mM **6** (at 7 μ s after laser flash). The inset shows the formation of benzofuranoxo radical at 610 nm in the peroxide solution containing 30 mM **6**.

tert-butyl peroxide in a 2:1 mixture (v/v) of the peroxide and benzene gives *tert*-butoxy radical, which reacts with 2(5*H*)-furanones (5–40 mM) giving rise to furanoxo radicals on microsecond time scales (eq 2–4). The related transient



spectra and growth kinetics are shown in Figure 4. Note the close similarity of the spectra consisting of three band systems (Figure 3, part D, and Figure 4, part A), attributable to furanoxo radical **10a** in acetonitrile and 1:2 benzene-di-*tert*-butyl peroxide, respectively. Based on eq 3 and 4, the pseudo-first-order rate constant (k_{obsd}) for the growth of transient absorption due to furanoxo radical is given by eq 5, where [S] represents the substrate concen-

$$k_{\text{obsd}} = k_d + k_H[\text{S}] \quad (5)$$

tration. Linear plots of k_{obsd} vs. [S] were used to determine k_H (as slopes). Also, comparison of absorbance changes due to the furanoxo radicals with those due to diphenylhydroxymethyl radical ($\epsilon_{\text{max}} = 3.2 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$ at 545 nm)¹⁰ obtained from diphenylmethanol as well as *p*-methoxyphenoxy radical ($\epsilon_{\text{max}} = 4.8 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$ at 405 nm)^{9b} enabled us to determine the extinction coefficients of the furanoxo radicals. The method is described elsewhere.^{9b} Data concerning hydrogen abstraction kinetics and furanoxo radical spectra are summarized in Table II.

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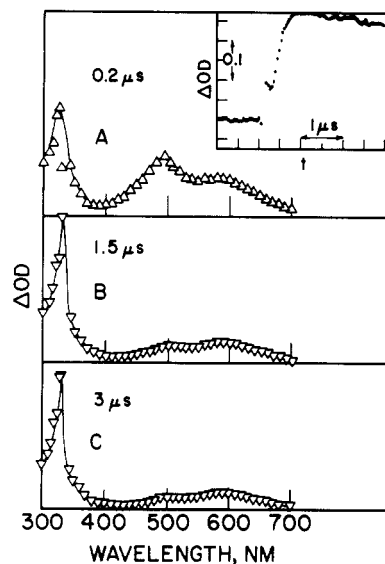
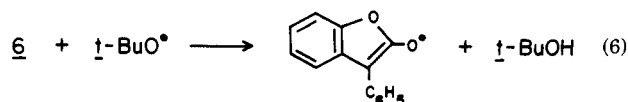


Figure 6. Transient absorption spectra at (A) 0.2, (B) 1.5, and (C) 3 μ s following 337.1-nm laser flash photolysis of 0.5 mM DCN in the presence of 24 mM **5c** in deoxygenated acetonitrile. The inset shows the growth of transient absorption at 325 nm (the distortion of the trace close to the laser pulse is due to scattered light).

As shown in Figure 5, part A, the furanoxo radical **10a** can also be produced by direct photolysis of the benzoyl derivative **3**. The formation of the radical in benzene upon 337.1-nm laser flash photolysis takes place within the laser pulse (~ 8 ns); this suggests that if the intermediacy of the triplet of **3**, the latter is very short lived (< 5 ns). Using benzophenone triplet formation for actinometry, the yield of radical formation under direct excitation of **3** is estimated at 0.55 ± 0.15 in degassed benzene; this value remains unchanged upon air saturation.

Under e.t. sensitization by $^1\text{DCN}^*$, furanone **2c** also shows transient spectra ($\geq 1 \mu$ s following laser flash) with structures and locations similar to those of furanoxo radical **10c** (Figure 4, part C). In this case, the growth process representing the transformation of the radical cation from **2c** to **10c** is observed at 360–400 nm. Also, there is decay of transient absorption at 420–450 nm due to both S^+ and $^3\text{DCN}^*$. Radical cations from bis(benzofuranones) **5b–d** produced by e.t. to $^1\text{DCN}^*$ behave similarly in terms of their fragmentation to benzofuranoxo radicals. As described for **5c** in Figure 6, the growth of transient absorption at 310–330 nm and concomitant decay at 450–700 nm over microseconds are ascribable to this process. Hydrogen abstraction by photogenerated *tert*-butoxy radical from benzofuranone **6** leads to the corresponding radical (eq 6) with an absorption spectrum (Figure 5, part B) very similar to those observed at $\geq 2 \mu$ s following the laser flash photolysis of DCN in the presence of **5b–d** in aerated acetonitrile. Furthermore, it has been shown earlier⁷ that direct photolysis of **5a–d** by 248 nm laser pulse results in $\text{C}_3\text{--C}_3'$ bond cleavage giving benzofuranoxo radicals; their spectra are identical with those observed for **5b–d** under DCN sensitization in the present study.



Laser flash photolysis of DCA at 425 nm in the presence of furanones **1e** and **2d** in acetonitrile gives rise to DCA $^-$ and S^+ with absorption spectra (Figure 7) that closely

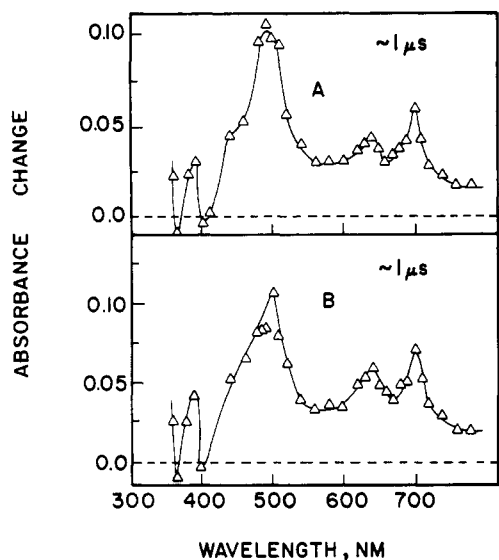


Figure 7. Transient absorption spectra at $\sim 1 \mu\text{s}$ following 425 nm laser flash photolysis of 0.2 mM DCA in deoxygenated acetonitrile containing (A) 43 mM **1e** and (B) 30 mM **2d**.

overlap each other. At 400–800 nm, the absorption spectrum of DCA^- (to be described elsewhere)¹¹ consists of three maxima at 505, 640, and 705 nm, the relative intensities at these wavelengths being 0.72, 0.65, and 1.0, respectively ($\epsilon_{\text{max}} = 8.0 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$ at 705 nm). As evident from Figure 7, the radical cations from **1e** and **2d** are spectrally similar to each other and contribute primarily at 450–510 nm (λ_{max} 490 nm). There is no indication in the case of **2d** that S^+ breaks apart into a furanoxo radical and benzyl carbonium ion.

(c) Decay and Quenching of Radicals and Radical Cations. Except in the cases of **2a–c**, the radical cations are found to decay by second-order or mixed kinetics in air-saturated acetonitrile. The initial portions (5–10 μs) of the decay of radical cations from **1a, b, d** at 390 or 700 nm could be fitted approximately into second-order, equal concentration kinetics. The rate constants ($k_{2,d}$) estimated for these processes are high ($5\text{--}7 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$), suggesting that charge neutralization of S^+ with the counter anion O_2^- is important. Small contributions from first-order processes, e.g., quenching by trace amounts of water in the solvent, can also render $k_{2,d}$'s artificially high. The decay of radical cations from **5b–d** at 490 nm could be fitted approximately into first-order kinetics with lifetimes (τ_{S^+}) close to 1 μs . Comparatively, the first-order decay of radical cations from **2a** and **2b** (at 700 nm) was faster ($\tau_{\text{S}^+} \sim 0.2 \mu\text{s}$). In the case of **2c**, τ_{S^+} was measured from the first-order growth of the furanoxo radical **10c** at 370 nm. τ_{S^+} data are summarized in Table I.

The quenching effects of several reagents, namely, water, methanol, and Br^- , were studied with **1a**, **2a**, and **5c** as the substrates. The pseudo-first-order rate constants (k_{obsd}) for S^+ decay (monitored at 700 nm for **1a** and **2a** and 490 nm for **5c**) were measured as functions of quencher concentrations ($[Q]$). The slopes of linear plots of k_{obsd} vs. $[Q]$ gave k_{q,S^+} (presented in Table III). Based on experiments in which the substrate concentrations were varied over 6–30 mM, the rate constants for dimerization of S^+ by interaction with respective ground states ($\text{S}^+ + \text{S} \rightarrow \text{S}_2^+$) were estimated to be small ($\leq 10^7 \text{ M}^{-1} \text{ s}^{-1}$ for S^+ from **1a** and **5c**).

Table I. Data Concerning DCN and DCA Singlet Quenching by 2(3H)-Furanones and Bis(benzofuranones) and Spectral/Kinetic Behavior of Radical Cations (Solvent Acetonitrile)

sensitizer	τ_{F} , ns	substrate	$K_{\text{sv}}^{\text{F},a}$, M^{-1}	$10^{10}k_{\text{a}}^{\text{ss}}$, $\text{M}^{-1} \text{ s}^{-1}$	δ_{ion}^b	$\lambda_{\text{max}}^{\text{S}^+,c}$, nm	$\tau_{\text{S}^+,d}$, μs
DCN	9.5	1a	140	1.5	0.5	390	
		1b	139	1.5	0.6	390	
		1c	142	1.5	0.3	430	
		1d	138	1.5	0.5	390	
		2a	129	1.4	0.5	390	0.22
		2b	161	1.7	0.3	390	0.18
		2c	168	1.8	0.4	440	2.9
		5a	~ 20	~ 0.2			
		5b	117	1.2	0.2	490	1.
		5c	106	1.1	0.2	490	0.9
DCA	15.7	5d	71	0.75	0.3	490	0.9
		1a	29	0.19			
		1c	187	1.2	0.2	430	
		1e	152	0.97	0.3	490	
		2a	49	0.31			
		2c	169	1.1	0.2	440	
		2d	179	1.1	0.4	490	

^a $\pm 15\%$. ^b $\pm 25\%$. ^c ± 5 nm; maxima at 600–750 nm or 300–330 nm are not included. ^d For decay by first-order kinetics (where applicable) in aerated acetonitrile.

Table II. Spectral and Kinetic Properties of Furanoxo Radicals in 1:2 Benzene-Di-*tert*-butyl Peroxide (v/v)

substrate	$10^7k_{\text{H}}^a$, $\text{M}^{-1} \text{ s}^{-1}$	λ_{max}^b , nm	$10^8\epsilon_{\text{max}}^c$, $\text{M}^{-1} \text{ cm}^{-1}$	$10^8k_{2,d}^a$, $\text{M}^{-1} \text{ s}^{-1}$
4a	2.0	370	16	6.2
		445	7.2	
		610 ^d	1.1	
4b	1.8	370	15	6.2
		450	7.8	
		620 ^d	1.6	
4c	2.0	370	12	6.2
		460	10	
		630 ^d	2.4	
6	2.0	330	14	8.1
		600	1.2	

^a $\pm 15\%$. ^b ± 5 nm. ^c $\pm 20\%$. ^d A minor vibronic peak belonging to the long wavelength band system is located at 550–570 nm (see Figures 4 and 5).

Table III. Rate Constants for the Quenching of Radical Cations in Acetonitrile

substrate	monitoring wavelength, nm	$k_{\text{q}}^{\text{S}^+}$, $\text{M}^{-1} \text{ s}^{-1}$ ^a		
		H_2O	MeOH	Br^- ^b
1a	700	1.0×10^6	8.0×10^5	2.9×10^{10}
2a	700	3.2×10^6	3.7×10^6	2.4×10^{10}
5c	490	7.4×10^5	3.9×10^6	2.2×10^{10}

^a $\pm 20\%$. ^b Added as tetra-*n*-propylammonium bromide.

The long-lived furanoxo radicals derived from **3**, **4a–c**, and **6** decay exclusively by second-order, equal concentration kinetics. From appropriate fits of kinetic traces over 70–80 μs (corresponding to 50–70% decay), we obtained the second-order rate constants ($k_{2,d}$) for decay in 1:2 benzene-di-*tert*-butyl peroxide. Linear plots of the reciprocal of absorbance against time gave $k_{2,d}/(\epsilon \cdot l)$ as slopes, where ϵ is the extinction coefficient of the radical at the monitoring wavelength and l is the pathlength of the cell (0.2 cm). The ϵ data in Table II were used in computing $k_{2,d}$. Note that $k_{2,d}$'s (Table III) are all smaller than the diffusion-controlled rate constant by about one order of magnitude. Under air saturation, the decay of the radicals becomes slightly enhanced but remains predominantly second order in nature. Approximate fits of kinetic traces under air saturation into second-order, equal concentration kinetics gave $k_{2,d}$ values 3–40% higher than

(11) Davis, H. F.; Bhattacharyya, K.; Das, P. K., manuscript in preparation.

those under deoxygenated conditions.

(d) Efficiency of Charge Separation. The efficiency of photoinduced charge separation was estimated in terms of the fraction (δ_{ion}) of sensitizer singlet quenching events that result in radical ions. The computation of ϕ_{ion} was based on absorbance changes due to radical anions of DCN and DCA monitored at 390 and 705 nm, respectively, and the contributions of radical cations (or radicals) were corrected for by using absorbance changes due to them measured in air-saturated solutions. With DCN as the sensitizer (λ_{ex} 425 nm) formation of thiocoumarin triplet in an optically matched benzene solution ($\phi_{\text{T}} = 1$, $\epsilon_{\text{max}}^{\text{T}} = 8.8 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$ at 485 nm)¹² were used for actinometry. Details of the method are given in previous publications.^{6c,8,13} The data regarding ϕ_{ion} are given in Table I. There is no indication of fast, e.t. induced C-C bond cleavage (homolytic) to benzyl and furanoxo radical in the case of **2a-c** or to two benzofuranoxo radicals in the case of **5b-d** (as we observed^{13,14} in recent studies on pinacols, pinacol ethers, and stilbene oxides).

Discussion

Based on the fluorescence spectra of DCN (onset at 350 nm) and DCA (0,0 band at 435 nm), their singlet energies ($\Delta E_{\text{S}_1-\text{S}_0}$) are estimated to be 3.54 and 2.85 eV, respectively (in acetonitrile). These combined with ground-state reduction potential data (-1.67 V vs. Ag/0.1 M AgNO₃ for DCN^{4a} and -0.87 V vs. SCE for DCA¹⁵) give 2.17 and 1.98 V as the reduction potentials ($*E_{1/2}^{\text{red}}$) of the singlets of DCN and DCA, respectively (both with respect to SCE). The free energy change ($\Delta G_{\text{e.t.}}$) for singlet mediated e.t. interaction is given by the Weller equation¹⁶ (below), where

$$\Delta G_{\text{e.t.}} = -*E_{1/2}^{\text{red}} + E_{1/2}^{\text{ox}} + W_{\text{p}} - W_{\text{r}} \quad (7)$$

$E_{1/2}^{\text{ox}}$ is the oxidation potential of the donor substrate and W 's are the electrostatic work in bringing together the product (or reactant) species to form an ion pair (or association complex). In the present case $W_{\text{r}} = 0$ and $W_{\text{p}} \cong -1 \text{ kcal/mol}$ (in acetonitrile). The fact that the furanones **1a** and **2a** quench ¹DCN* with k_{q}^{ss} in the limit of diffusion control and ¹DCA* with k_{q}^{ss} below the limit of diffusion control (Table I) suggests¹⁷ that $-\Delta G_{\text{e.t.}}$ is $\geq 10 \text{ kcal/mol}$ in the former case and $\leq 5 \text{ kcal/mol}$ in the latter case. Thus, from eq 7, $E_{1/2}^{\text{ox}}$ of furanones **1a** and **2a** is estimated to be 1.8 V (vs. SCE), that is, slightly below $E_{1/2}^{\text{ox}}$ of styrene (experimental value close to 2.0 V in acetonitrile, vs. SCE).^{19a} Compared to **1a** and **2a**, furanones **1c** and **2c** quench DCA fluorescence with much higher k_{q}^{ss} ($\sim 1 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$, Table I). A relatively low value ($\sim 1.6 \text{ V}$ vs. SCE) is estimated for $E_{1/2}^{\text{ox}}$ of **1c** and **2c** and appears to be associated with the *p*-anisyl group^{19b} at the 3-position (rather than the styryl moiety).

With **1a-d** as donors for ¹DCN* and **1e** and **d** as donors for ¹DCA*, the transient spectra observed in aerated acetonitrile following the decay of cyanoaromatic radical anion and triplet (in the case of DCN) are attributable to the radical cations of the substrates in which the furanone

rings appear to remain in tact. That decarbonylation, or cleavage of a vulnerable bond (C₂-C₃ or C₂-O), does not occur in these radical cations on our time scale is indicated by the following. First, when observed close to the laser pulse, the transient spectra of radical cations that act as precursors for furanoxo radicals in the case of **2a-c** show close resemblance to those observed in the case of **1a-c**, respectively. Second, the radical cations from **1a-c** and **2d** are relatively long lived and decay predominantly by second-order, equal concentration kinetics; no growth/decay phenomena, ascribable to rupture of bond(s), are observed in terms of transient absorption on a nanosecond to microsecond time scale (this, however, does not rule out the possibility of fast bond cleavage in radical cations within the laser pulse). Third, among **1a**, **1b**, and **1c** and between **1e** and **2d**, there is practically no dissimilarity in the radical cation spectra. Ring-opened radical cations with a carbocationic or radical center at C³ or radical cations of decarbonylation products (α,β -unsaturated ketones) would have absorption spectra sensitive to the number of phenyl substituents at C₃ (**1e** vs. **2d**) and to electron donor/acceptor groups at the para position of the phenyl substituent at C₃ (**1a**, **1b**, and **1d**). The absorption spectrum of the radical cation from **1c** (λ_{max} 430 nm) differ significantly from those from **1a,b,d** (λ_{max} 390 nm), but this is understandable by the fact that the radical cation center in the former case is localized on the *p*-anisyl group (giving rise to spectra similarity with *p*-methoxytoluene radical cation).

The facile fragmentation of radical cations derived from **2a-c** to furanoxo radicals is reminiscent of similar behavior previously reported^{6b,c} for phenyl glycopyranosides. The radical cations from the latter undergo transformation to phenoxo radicals and glycopyranoside-related carbonium ions. Interestingly, the kinetics of fragmentation is much slower for **2c** (relative to **2a** and **2b**, see τ_{S^+} data in Table I). A reasonable explanation for this difference is that $E_{1/2}^{\text{ox}}$ is lower for **2c** than for **2a** or **2b** (that is, the corresponding radical cation is more stable), and thus the free energy change associated with intramolecular electron transfer causing C-C bond cleavage (eq 1) is less negative in the case of **2c**. A similar reasoning in terms of unfavorable free energy change can also be advanced for the lack of fragmentation in the case of furanone **2d** (relative to **2a-c**).

As evident from δ_{ion} data in Table I, the efficiencies of net e.t. in the course of quenching processes are modest (0.2-0.6). However, the behavior of radical cations from 2(*3H*)-furanones suggest that there would be little or no decarbonylation¹⁸ through their intermediacy. There is a possibility of cyclization in the radical cations from **1e** and **2d** leading to oxidized forms (one-electron) of dihydrophenanthrenes. However, whether decarbonylation and phenanthrene formation (seen⁷ under direct photolysis) occur to an appreciable extent under e.t. sensitization remains to be established by studies¹⁸ based on steady-state irradiation and product isolation. In the case of bis(benzofuranones) (**5a-d**) under direct excitation⁷, the benzofuranoxo radicals are the primary intermediates leading to the isolable photoproducts. The finding that these radicals are also formed via fragmentation of the radical cations under e.t. sensitization suggests that pho-

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(18) A preliminary study with **1a** as the substrate under steady-state sensitization by DCN in acetonitrile ($\lambda_{\text{ex}} \geq 320 \text{ nm}$) has shown the lack of formation of the decarbonylation product.

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tochemistry of bis(benzofuranones) would be similar under both conditions of excitation.

Experimental Section

All melting points are uncorrected and were determined on a Mel-Temp melting point apparatus. The IR spectra were recorded on Perkin-Elmer Model 377 or Model 580 infrared spectrophotometers. The electronic spectra were recorded on Cary 17D, Cary 219, or Beckman DB spectrophotometers.

Starting Materials. Purification and sources of solvents and reagents for laser studies and e.t. reactions are available in previous publications^{7-9,13,20,21} on related subjects.

Furanones 1a, 1e, 2d, 3, and 4a-c, Benzofuranone, 6, and Bis(benzofuranones) 5a-d. 3,3,5-Triphenyl-2(3*H*)-furanone (1a),²³ mp 120–121 °C, 3,3,4,5-tetraphenyl-2(3*H*)-furanone (1e),²³ mp 137–138 °C, 3-benzyl-3,4,5-triphenyl-2(3*H*)-furanone (2d),²⁴ mp 154 °C, 3-benzoyl-3,5-diphenyl-2(3*H*)-furanone (3),²⁵ mp 186 °C, 3,5-diphenyl-2(5*H*)-furanone (4a),²⁶ mp 107–108 °C, 3-(4-methylphenyl)-5-phenyl-2(5*H*)-furanone (4b),²⁶ mp 104–105 °C, 3-(4-methoxyphenyl)-5-phenyl-2(5*H*)-furanone (4c),²⁶ mp 98–99 °C, 3-phenylbenzo[*b*]-2(3*H*)-furanone (6),²⁷ mp 113–114 °C, 3,3'-diphenyl-3,3'-dibenzo[*b*]furan-2,2'-(3*H*,3'*H*)-dione (5a),²⁸ mp 175–176 °C, 5,5'-dimethyl-3,3'-diphenyl-3,3'-dibenzo[*b*]furan-2,2'-(3*H*,3'*H*)-dione (5b),²⁸ mp 201–202 °C, 6,6'-dimethyl-3,3'-diphenyl-3,3'-dibenzo[*b*]furan-2,2'-(3*H*,3'*H*)-dione (5c),²⁸ mp 170–171 °C, and 7,7'-dimethyl-3,3'-diphenyl-3,3'-dibenzo[*b*]furan-2,2'-(3*H*,3'*H*)-dione (5d),²⁸ mp 229–230 °C, were prepared by reported procedures.

2(3*H*)-Furanones, 1b-d. A general procedure for the preparation of 1b-d involved the heating of the appropriate but-2-ene-1,4-dione (9a-c,d) around 300 °C in a sealed tube for 1–1.5 h and workup of the mixture by extraction with methylene chloride, chromatographing over silica gel (elution with petroleum ether or benzene), followed by recrystallization from suitable solvents.

The but-2-ene-1,4-diones, 9a-d were prepared through the condensation of the appropriate benzil derivative (7a-d) with acetophenone in the presence of potassium hydroxide in ethanol. In a typical experiment, a mixture of 0.025 mol of the benzil derivative (7), 0.027 mol of acetophenone, and 1 g of powdered potassium hydroxide in 30 mL of ethanol was stirred around 50–60 °C for 15 min and later kept in a refrigerator for a couple of days. The solid product that separated out was filtered and recrystallized from suitable solvents.

1,4-Diphenyl-2-(*p*-tolyl)but-2-ene-1,4-dione (9b). 9b was obtained in a 63% yield, mp 145–146 °C, after recrystallization from ethanol: IR ν_{\max} (KBr) 3060 and 2850 (CH), 1660 and 1655 (C=O) and 1600 (C=C) cm^{-1} ; ¹H NMR (CCl₄) δ 2.25 (s, 3 H, methyl, 7.25 (m, 15 H, aromatic and vinylic).

Anal. Calcd for C₂₃H₁₈O₂: C, 84.66; H, 5.52. Found: C, 84.26; H, 5.16.

3,5-Diphenyl-3-(4-methylphenyl)-2(3*H*)-furanone (1b). 1b was obtained in a 60% yield, mp 109–110 °C, after recrystallization from ethanol: IR ν_{\max} (KBr) 3120, 3040, 3025 and 2910 (CH), 1780 (C=O), 1660 and 1600 (C=C) cm^{-1} ; UV λ_{\max} (methanol) 248 nm (ϵ 6400), 270 (12,800); ¹H NMR (CCl₄) δ 2.33 (s, 1 H, methyl), 6.3 (s, 1 H, vinylic), 7.4 (m, 14 H, aromatic).

Anal. Calcd for C₂₃H₁₈O₂: C, 84.66; H, 5.52. Found: C, 84.60; H, 5.12.

1,4-Diphenyl-2-(4-methoxyphenyl)but-2-ene-1,4-dione (9c).

9c was obtained in a 51% yield, mp 104–105 °C, after recrystallization from methanol: IR ν_{\max} (KBr) 3060, 2960 and 2820 (CH), 1655 and 1640 (C=O), 1600 (C=C) cm^{-1} ; ¹H NMR (CCl₄) 3.75 (s, 3 H, methoxy), 7.4 (m, 15 H, aromatic and vinylic).

Anal. Calcd for C₂₃H₁₈O₃: C, 80.70; H, 5.26. Found: C, 80.56; H, 5.10.

3,5-Diphenyl-3-(4-methoxyphenyl)-2(3*H*)-furanone (1c). 1c was prepared in a 50% yield, mp 92–93 °C, after recrystallization from ethanol: IR ν_{\max} (KBr) 3120, 3060, 2840 (CH), 1780 (C=O), 1610 (C=C) cm^{-1} ; UV λ_{\max} (methanol) 247 nm (ϵ 7300), 271 (12,400); ¹H NMR (CCl₄) 3.75 (s, 3 H, methoxy), 6.3 (s, 1 H, vinylic), 7.15 (m, 14 H, aromatic).

Anal. Calcd for C₂₃H₁₈O₃: C, 80.70; H, 5.26. Found: C, 80.60; H, 5.08.

1,4-Diphenyl-2-(4-cyanophenyl)but-2-ene-1,4-dione (9e).

A mixture of *p*-bromobenzil (5.5 g, 0.02 mol), acetophenone (2.6 g, 0.021 mol), and potassium hydroxide (0.75 g) in ethanol (40 mL) was stirred around 40 °C for 30 min and worked up in the usual manner to give a mixture (4.0 g, 53%, mp 90 °C) of 1,4-diphenyl-2-(4-bromophenyl)but-2-ene-1,4-dione (9d) (major) and 2,4-diphenyl-1-(4-bromophenyl)but-2-ene-1,4-dione (minor). This mixture (3.91 g, 0.01 mol) was combined with cuprous cyanide (2.68 g, 0.03 mol) and stirred in refluxing dimethylformamide (DMF) for 5 h. The reaction mixture was poured into hot aqueous sodium cyanide solution (25 mL) and extracted with benzene. Removal of the solvent from the benzene layer gave a residual solid, which was chromatographed over silica gel. Elution with a mixture (8:2) of benzene and petroleum ether gave 300 mg (9%) of 2,4-diphenyl-1-(4-cyanophenyl)but-2-ene-1,4-dione, mp 142–143 °C (minor product). Further elution with benzene gave 1.8 g (53%) of 1,4-diphenyl-2-(4-cyanophenyl)but-2-ene-1,4-dione (9e): mp 178–179 °C; IR λ_{\max} (KBr) 3100 and 3070 (CH), 2240 (C≡N), 1675 and 1660 (C=O), 1600 (C=C) cm^{-1} ; ¹H NMR (CDCl₃) δ 7.6 (m, aromatic and vinylic).

Anal. Calcd for C₂₃H₁₅NO₂: C, 81.89; H, 4.45; N, 4.15. Found: C, 82.01; H, 4.80; N, 4.20.

3,5-Diphenyl-3-(4-cyanophenyl)-2(3*H*)-furanone (1d). 1d was obtained in a 50% yield, mp 114–115 °C, after recrystallization from a mixture (1:1) of carbon tetrachloride and petroleum ether: IR ν_{\max} (KBr) 3100, 3050 and 3030 (CH), 2215 (C≡N), 1780 (C=O), 1650 and 1600 (C=C) cm^{-1} ; UV λ_{\max} (methanol) 240 nm (ϵ 22,700), 270 (21,600); ¹H NMR (CCl₄) δ 6.2 (s, 1 H, vinylic), 7.2 (m, 14 H, aromatic).

Anal. Calcd for C₂₃H₁₅NO₂: C, 81.89; H, 4.45; N, 4.15. Found: C, 82.19; H, 4.95; N, 4.37.

2(3*H*)-Furanones, 2a-c. A general procedure was to heat a mixture of the appropriate 2(5*H*)-furanone (4a-c) (0.02 mol) and sodium hydride (0.021 mol) in dry tetrahydrofuran (THF) to around 50–60 °C, till the solution became clear yellow. The mixture was then cooled and benzyl benzenesulfonate (0.02 mol) was added gradually. After stirring at room temperature for 20 h, the precipitated sodium salt was filtered off and washed with ether. The combined ether-THF filtrate was evaporated under vacuum and the product was recrystallized from suitable solvents.

3-Benzyl-3,5-diphenyl-2(3*H*)-furanone (2a) was obtained in nearly quantitative yield, mp 148 °C, after recrystallization from methanol: IR ν_{\max} (KBr) 3120, 3080, 3060, 3040, 2920 (CH), 1780 (C=O), 1650 and 1595 (C=C) cm^{-1} ; ¹H NMR (CDCl₃) δ 3.55 (s, 2 H, methylene), 6.27 (s, 1 H, vinylic), 7.5 (m, 15 H, aromatic).

3-Benzyl-3(4-methylphenyl)-5-phenyl-2(3*H*)-furanone (2b) was obtained in a 62% yield, mp 164–165 °C, after recrystallization from ethanol: IR ν_{\max} (KBr) 3110, 3080, 3060, 3025, 2920 and 2850 (CH), 1780 (C=O), 1650 and 1600 (C=C) cm^{-1} ; UV λ_{\max} (methanol) 251 nm (ϵ 9400), 268 (13,600); ¹H NMR (CDCl₃) δ 2.35 (s, 3 H, methyl), 3.43 (s, 2 H, methylene), 6.07 (s, 1 H, vinylic), 7.3 (m, 14 H, aromatic).

Anal. Calcd for C₂₄H₂₀O₂: C, 84.70; H, 5.88. Found: C, 84.77; H, 5.82.

3-Benzyl-3-(4-methoxyphenyl)-5-phenyl-2(3*H*)-furanone (2c) was obtained in a 70% yield, mp 138–139 °C, after recrystallization from ethanol: IR ν_{\max} (KBr) 3120, 3060, 3025, 2920 and 2840 (CH), 1780 (C=C), 1650 and 1605 (C=C) cm^{-1} ; ¹H NMR (CDCl₃) δ 3.33 (s, 2 H, methylene), 3.75 (s, 3 H, methoxy), 6.0 (s, 1 H, vinylic), 7.2 (m, 14 H, aromatic).

Anal. Calcd for C₂₀H₂₀O₃: C, 80.90; H, 5.62. Found: C, 81.07; H, 5.28.

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Fluorescence Measurements. The steady-state fluorescence measurements were performed in a right-angle geometry with a spectrofluorimeter from SLM; a description of this apparatus has been given in a previous publication.²⁰

Laser Flash Photolysis. For laser flash photolysis, excitation was carried out in a front-face configuration with 337.1-nm laser pulses (8 ns, 2-3 mJ) from a Molelectron UV-400 system or 425-nm laser pulses (6 ns, 2-10 mJ), generated by pumping a methanolic solution of stilbene 420 (Exciton) with the output at third harmonic (354 nm) from a Quanta-Ray Nd-YAG system. The details of the kinetic spectrometer and computerized data collection system are available elsewhere.²⁰⁻²² Rectangular quartz cells with 2- or 3-mm path lengths along the direction of the analyzing light were used for laser flash photolysis. Deoxygenation of solutions was effected by saturating them with argon.

Registry No. 1a, 2313-03-3; 1a⁺, 97861-48-8; 1b, 97861-35-3; 1b⁺, 97861-49-9; 1c, 97861-36-4; 1c⁺, 97861-50-2; 1d, 97861-37-5; 1d⁺, 97861-51-3; 1e, 6963-25-3; 1e⁺, 97877-61-7; 2a, 97861-38-6; 2a⁺, 97861-43-3; 2b, 97861-39-7; 2b⁺, 97877-60-6; 2c, 97861-40-0; 2c⁺, 97861-44-4; 2d, 92545-46-5; 2d⁺, 97877-62-8; 3, 31994-73-7; 4a, 5369-56-2; 4b, 97861-41-1; 4c, 97861-42-2; 5a, 65425-10-7; 5b, 65425-11-8; 5b⁺, 97861-45-5; 5c, 65425-12-9; 5c⁺, 97861-46-6; 5d, 65425-05-0; 5d⁺, 97861-47-7; 6, 3117-37-1; 7a, 134-81-6; 7b, 2431-00-7; 7c, 22711-21-3; 7d, 39229-12-4; 8, 98-86-2; 9a, 5435-97-2; 9b, 88406-92-2; 9c, 88406-93-3; 9d, 88406-95-5; 9e, 88406-97-7; 10a, 97861-52-4; 10b, 97861-53-5; 10c, 97861-54-6; DCN, 3029-30-9; DCA, 1217-45-4; *t*-BuO[•], 3141-58-0; H[•], 12385-13-6; *p*-BrC₆H₄COC(C₆H₅)=CHCOC₆H₅, 97861-56-8; *p*-CNC₆H₄COC(C₆H₅)=CHCOC₆H₅, 97861-57-9; 3-phenyl-2-benzofuranoxo radical, 97861-55-7.

New Synthetic Methods. Conjugate Addition of Alkyl Groups to Electron Deficient Olefins with Nitroalkanes as Alkyl Anion Equivalents¹

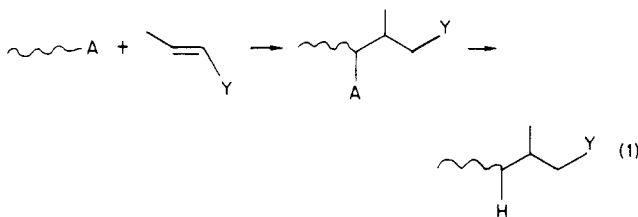
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The sequence of the Michael addition of nitroalkanes and denitration from the adduct provides a new and general method for conjugate addition of primary and secondary alkyl groups to electron deficient olefins such as α,β -unsaturated aldehydes, ketones, esters, nitriles, sulfoxides, and sulfones.

Conjugate addition of alkyl groups to electron deficient olefins is a highly useful reaction as basic strategy for organic synthesis. Although direct addition of organometallics to electron deficient olefins is straightforward, it cannot be applied to all kinds of cases.^{2,3} To compensate the defects of the direct method, an indirect method using an activating group, A, as in eq 1 has also been used extensively. As organo sulfur groups stabilize an adjacent carbanion effectively and also they are readily removed, they have been used most frequently among various kinds of A.⁴ In this paper we wish to report the nitro group to be the best A in eq 1. Namely, the nitro group stabilizes an adjacent carbanion more effectively and is removed more selectively than any other groups.



Y = electron withdrawing group
A = SR, SOR, SO₂R, CN, NO₂ etc.

Results and Discussion

A new method for conjugate addition consists of the sequence of two steps, the Michael addition of nitroalkanes and denitration from the adduct. The novelty of a new method lies in the second step, replacement of the nitro group by hydrogen. This type of reaction has been found in recent years,⁵ and five methods are available so far.⁶ Among them, the method using tributyltin hydride is the only one reliable method to be applied to denitration of the Michael adduct.⁷

Conjugate Addition of Secondary Alkyl Groups. The Michael addition of secondary nitro compounds and the subsequent removal of the nitro group from the adduct provide a new and general method for conjugate addition of secondary alkyl groups to electron deficient olefins (eq 2). The results are summarized in Table I. Three typical examples are selected and shown in eq 3, 4, and 5. The first example is the conjugate addition of the 2-octyl group to methyl vinyl ketone. The first step was simply done by mixing 2-nitrooctane, methyl vinyl ketone, and tetramethylguanidine (TMG, 0.1 equiv)⁸ in acetonitrile at room

(5) First clean denitrohydrogenation was reported in 1978 by N. Kornblum, where MeSNa was used as a reducing agent: Kornblum, N.; Carlson, S. C.; Smith, R. G. *J. Am. Chem. Soc.* 1978, 100, 289; *Ibid.* 1979, 101, 647.

(6) Method A, the use of MeSNa in dipolar aprotic solvents.⁵ Method B, the use of KOH in ethylene glycol: Krasuska, A. L.; Pitrowska, H.; Urbanski, T. *Tetrahedron Lett.* 1979, 1243. Method C, the use of 1-benzyl-1,4-dihydronicotinamide: Ono, N.; Tamura, R.; Kaji, A. *J. Am. Chem. Soc.* 1980, 102, 2581; *Ibid.* 1983, 105, 4017. Method D, the present method using Bu₃SnH.¹ Independently Tanner reported that some kinds of tertiary nitro groups were replaced by hydrogen with Bu₃SnH: Tanner, D. D.; Blackburn, E. V.; Diaz, D. D. *J. Am. Chem. Soc.* 1981, 103, 1557. Method E, the use of NaTeH: Suzuki, H.; Takaoka, K.; Osuka, A. *Bull. Chem. Soc. Jpn.* 1985, 58, 1067.

(7) The nitro compounds used for denitration in ref 6 were mostly tertiary and activated compounds. In fact it was reported that NaTeH was unable to replace the nitro groups of 3 in Table I by hydrogen.⁶ Bu₃SnH is the best reagent so far for replacing the nitro group by hydrogen.¹

(8) Giuli, D.; Barco, G.; Pollini, G. P. *Synthesis*, 1972, 45.

(1) Preliminary report of this work: Ono, N.; Miyake, H.; Tamura, R.; Kaji, A. *Tetrahedron Lett.* 1981, 22, 1705.

(2) (a) Posner, G. H. *Org. React.* 1972, 19, 1. (b) House, H. O. *Acc. Chem. Res.* 1976, 9, 59. (c) Yamamoto, Y.; Yamamoto, S.; Yatagai, H.; Ishihara, Y.; Maruyama, K. *J. Org. Chem.* 1982, 47, 119. (d) Clive, D. L. J.; Farina, V.; Beaulieu, P. L. *Ibid.* 1982, 47, 2572. (e) Lipshutz, B. H.; Wilhelm, R. S.; Kozlowski, J. A. *Ibid.* 1984, 49, 3938.

(3) Although conjugate addition of organometallic reagents to α,β -unsaturated carbonyl compounds has been well studied, other types of conjugate addition are little known, see ref 2.

(4) (a) Magnus, P. D. *Tetrahedron* 1977, 33, 2019. (b) Block, E. "Reactions of Organosulfur Compounds"; Academic Press: New York, 1978. (c) Stowell, J. C. "Carbanions in Organic Synthesis"; John Wiley and Sons: New York, 1979.