J. Am. Chem. Soc. **1989**, *111*, 1337-1343

Electron and Hydrogen Atom Transfer Mechanisms for the Photoreduction of *o*-Quinones. Visible Light Induced Photoreactions of *β*-Lapachone with Amines, Alcohols, and Amino Alcohols

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Received June 30, 1988

Abstract: *β*-Lapachone (**1**), a substituted *o*-naphthoquinone absorbing into the visible (λ_{max} = 424 nm in benzene), is cleanly and efficiently reduced to the corresponding semiquinone radical upon photolysis in degassed solutions with alcohols, amines, and *β*-amino alcohols. The course and products of these photoreactions have been followed by NMR, ESR, fluorescence, and absorption spectroscopy. For all three types of reductant the overall reaction involves $2e^-$ oxidation of the donor, and the quantum efficiencies show a dependence upon quinone concentration indicative of the role of a second dark reduction of **1** by products of the primary photolysis. For amines and amino alcohols the reaction is initiated by single electron transfer quenching of triplet **1**. For triethylamine the mechanism is indicated to be a sequence of two electron transfer–proton transfer steps culminating in two semiquinone radicals and the enamine $Et_2NCH{=}CH_2$. For amino alcohols a C–C cleavage concurrent with deprotonation of the alcohol (oxidative photofragmentation) occurs, in competition with reverse electron transfer, following the quenching step. For both amines and amino alcohols, limiting efficiencies of reaction approach 2 (for $QH^{\bullet}$ formation). In contrast, both 2-propanol and benzyl alcohol are oxidized by excited states of **1** with much lower efficiency. The probable mechanism for photooxidation of the alcohols involves a H atom abstraction quenching of the excited state followed by an electron transfer–proton transfer sequence in which a ground-state **1** is reduced. Lower limiting efficiencies for photoreduction of **1** by the alcohols are attributed to inefficiencies of net H-atom transfer in the quenching step.

Numerous studies over several decades have involved diverse quinone derivatives as key reagents in photoredox processes ranging from relatively simple excited state quenching events to complex multistep processes such as photosynthesis.[3-5] Different quinones have been shown to serve as excited substrates, quenchers, or secondary relays just as a variety of reduced forms of these quinones—ion or neutral radicals or stable or metastable multielectron-reduction products or various addition products—have been implicated as transient or permanent photoproducts in these reactions.[6-10] Among the most interesting quinones, as far as their potential chemistry as excited substrates is concerned, are *o*-quinones such as phenanthrenequinone or 1,2-naphthoquinone; these molecules share the features of *α*-diketones, prominent absorption in the visible ($\lambda > 400$ nm), with the general redox properties of quinones, and thus relatively rich and efficient photoreactivity from low-energy excitation would be anticipated. Previous studies of the photoreactivity of *o*-quinones have demonstrated that for compounds such as phenanthrenequinone efficient intersystem crossing occurs, following photoexcitation, to produce a moderately long-lived (μs) triplet having reactivity characteristic of cyclic *α*-diketones such as camphorquinone.[11,12]

The chemically reactive triplet state could be expected to participate in either carbonyl or aromatic type excited-state processes. Evidence for a prominent role of H-atom abstraction has been obtained in several investigations.[13-15] Studies by Farid and co-workers, Maruyama et al., Rubin, and others have demonstrated that addition reactions occur prominently when phenanthrenequinone and naphthoquinone are irradiated in the presence of alkenes; for electron rich alkenes such as 2,3-dimethyl-2-butene or xanthene a variety of cycloadducts are formed together with smaller amounts of reductive photoadducts, which are most easily attributed to coupling of intermediate radicals.[16-18] It is also found that the structure of the stable photoadducts depends on the nature of the solvent used.[19-21] Although triplet quinones should be good electron acceptors, there are relatively few examples which show clear cut cases of quenching of *o*-quinones excited states by single-electron transfer.[22]

In the present paper we report results of a study of the photoreactions of the *o*-quinone *β*-lapachone (**1**), with tertiary amines, *α*-amino alcohols, and alcohols. The results of these studies contrast with earlier studies of *o*-quinone photoreactivity; in the present cases, the primary photoreaction is shown to be a direct photoredox process involving either electron transfer or H atom abstraction quenching of the quinone excited state to generate a relatively stable, semireduced quinone radical, $QH^{\bullet}$. These studies demonstrate that for **1** the semireduced product is formed in relatively high efficiency and, in most cases, with reasonable stability, provided oxygen is excluded.

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Table I. Maximum Absorbance of β-Lapachone in Various Solvents

	benzene	CH_2Cl_2	2-propanol	CH_3COCH_3	CH_3CN	DMSO
ϵ[a]	2.27	8.9	18.3	20.7	37.5	46.6
λ_{max}, nm	424	425	428	430	434	438

[a] Dielectric constant.

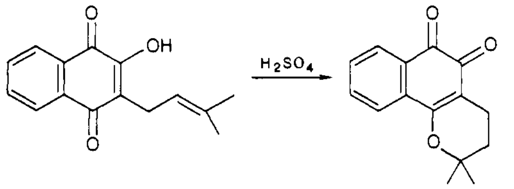
Table II. Reduction Potential of Electron Acceptors

electron acceptors	$E_{1/2(A/A^-)}$ vs SCE	$E^s_{(0-0)}$, eV	$E^s_{1/2(A^\bullet/A^-)}$	$E^T_{(0-0)}$, eV	$E^T_{1/2(A^\bullet/A^-)}$
β-lapachone	−0.787[a]	2.92	2.15	1.99	1.21
phenanthraquinone	−0.625,[a] −0.66[b]	3.02	2.36	2.11	1.46
naphthoquinone	−0.544,[a] −0.56[b]	3.12	2.54		
thioindigo	−0.45[a]	2.22	1.82		
oxalylindigo	−0.415[a]	2.84	2.43		

[a] Measured value. [b] (1) Peover, M. E. *J. Chem. Soc.* **1962**, 4540. (2) Bezuglyi, B. D.; Kheifets, L. Ya; Zakhs, E. R.; Efros, L. S. *J. Org. Chem. USSR* (*Engl. Transl.*) **1966**, *2*, 1096.

Results

Most of the studies in the present paper have involved the *o*-quinone β-lapachone (**1**) as the excited-state substrate; however, comparative investigations have shown that in most cases the structurally related oxalylindigo (**2**) and phenanthrenequinone exhibit comparable reactivity while 1,2-naphthoquinone in many cases does not. β-Lapachone can be obtained by sulfuric acid treatment of the natural *p*-quinone lapachol[23] (from the Brazilian wood Bignoniaceae, eq 1) or from synthetic procedures.[24] All four of the *o*-quinones show moderately strong (ϵ 100–1000) transitions in the visible spectra and a stronger band in the UV; for β-lapachone the visible band shows a red shift with an increase in solvent polarity (Table I). β-Lapachone is characterized by a greatly increased solubility in most organic solvents compared to the two unsubstituted aromatic quinones. In common with other *o*-quinones, β-lapachone exhibits very weak fluorescence with a maximum near 482 nm in benzene; the fluorescence is essentially unaffected by degassing solutions via argon bubbling or more rigorous freeze–pump–thaw cycles. A metastable species can be detected upon laser excitation by time-resolved photoacoustic calorimetry which can be attributed to the triplet of **1**; the energy of this species is measured as 46 kcal/mol, which is in good agreement with the 48.8 kcal/mol reported for phenanthrenequinone.[25] The lifetime for the β-lapachone triplet in argon-degassed benzene is in the range 400–600 ns. Table II compares reduction potentials for **1** and related *o*-quinones with those for other quinone type molecules such as thioindigo and oxalylindigo, which have been used as visible light absorbing reagents in related photoredox studies.[26,27] As the data in Table II indicate, the *o*-quinones should be reactive acceptors in both excited singlet and triplet states.



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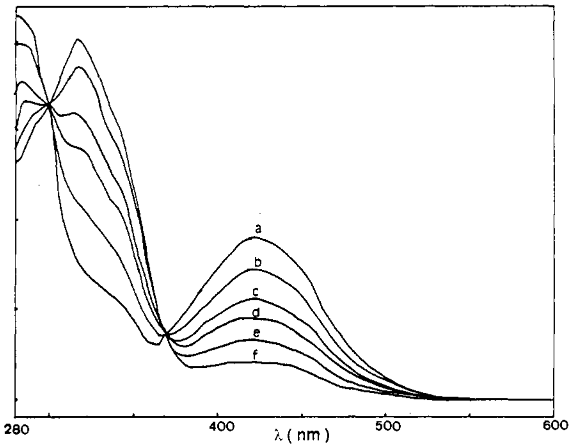

Figure 1. Photoreduction of β-lapachone (5 × 10^{-4} M) by triethylamine (0.02 M); spectral changes observed upon irradiation in benzene (a, 0 min; b, 0.5 min; c, 1 min; d, 1.5 min; e, 2 min).

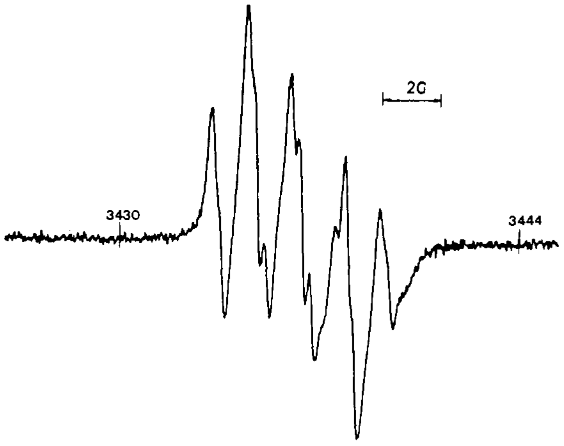

Figure 2. ESR spectrum observed during irradiation of β-lapachone/triethylamine in benzene. The same spectrum is also observed during irradiation of β-lapachone/*erythro*-MDBOH and after stopping irradiation for 30 min at room temperature in either benzene or CH_2Cl_2; microwave frequency 9640 mHz, microwave attenuation 24, modulation amplitude 0.02, centerfield 3435.57 Hz.

Table III. Quantum Yields of Photoreduction of β-Lapachone by Amine Donors

	4[a]	**5**[a]	TEA[b]	DABCO[c]
ϕ_{red}[d]	1.454	0.398	1.478	0.02

[a] **4** is *erythro*-MDBOH, and **5** is *threo*-MDBOH. [b] TEA is triethylamine. [c] DABCO is triethylenediamine. [d] [β-Lapachone] = 5 × 10^{-4} M, [donor] = 0.05 M, samples were vacuum degassed, and quantum yields were measured in benzene.

Photoreaction of β-Lapachone with Amines. Irradiation of β-lapachone in the presence of tertiary amines such as triethylamine in degassed solutions of organic solvents (e.g. benzene, methylene chloride, acetonitrile) leads to rapid, efficient bleaching of the long-wavelength transitions of **1** together with a buildup

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(23) If lapachol is dissolved in concentrated sulphuric acid and then poured into water, β-lapachone is precipitated, but when lapachol is treated with hydrochloric acid, the α-isomer is formed. Similarly, concentrated sulphuric acid converts α-lapachone into the β-lapachone and the process is reversed in concentrated hydrochloric acid. All these reactions are virtually quantitative. The detailed information is given in the following references: (a) Hooker, S. C. *J. Chem. Soc.* **1892**, *61*, 611. (b) Hooker, S. C. *Ibid.* **1896**, *69*, 1355.

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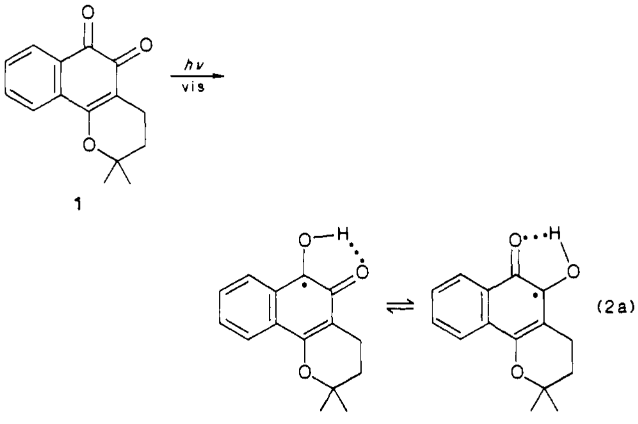
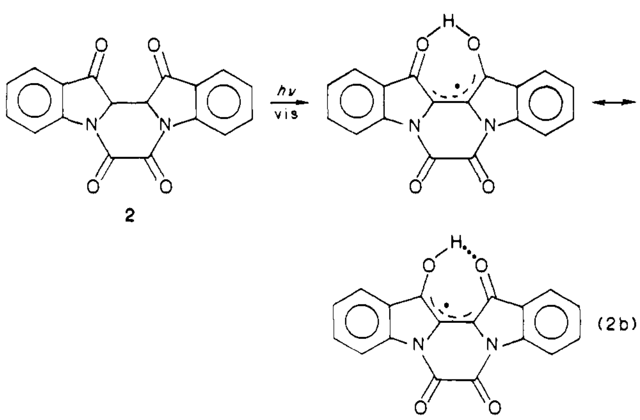
of a new absorptions near 320 nm (Figure 1, Table III). When the reaction is followed by ESR, the buildup of a single radical species (Figure 2) is observed concurrent with the changes in the UV–vis spectrum. For several solvent–amine combinations the ESR spectrum is indefinitely stable and approximately the same spectrum and total intensity are observed over a range of temperatures (−70 to 25 °C). The 5-line ESR spectrum ($g = 2.0037$) obtained is readily attributed to the semireduced radical **3**, $QH^\bullet$, which is stable in the absence of oxygen, but rapidly disappears on exposure to air to regenerate **1** quantitatively. A similar result was observed in previous studies with the *o*-quinone-related oxalylindigo (eq 2).[21,26] The stability of $QH^\bullet$ in solution can be attributed to an unfavorable equilibrium for disproportionation (eq 3). Interestingly, the hydroquinone from **1**, QH_2, can be





$$2QH^\bullet \rightarrow Q + QH_2 \qquad (3)$$

obtained by $LiAlH_4$ reduction in anhydrous ethyl ether; the hydroquinone is reasonably stable at room temperature in the air but slowly oxidizes to **1** (via **3**) upon standing in the dark. The hydroquinone exhibits a strong fluorescence at 398 nm which is not seen at all in solutions of **1** irradiated with triethylamine or the other reductants used in these investigations. The presence of clean isosbestic points in the absorption spectra throughout the irradiation and the quantitative regeneration of **1** upon exposure of irradiated solutions to O_2 indicate that the predominant, if not exclusive, reaction of **1** upon irradiation with Et_3N is reduction to the semiquinone (eq 2a). Amine oxidation products are more difficult to determine, due likely to their instability,[28,29] however, photolysis of **1** and Et_3N in degassed C_6D_6 in an NMR tube leads to the appearance of new proton resonances at 5.75 (triplet, 1 H), 3.19 (doublet, 2 H), 2.72 (quartet, 4 H), and 0.96 ppm (triplet, 6 H) assigned to the enamine, $Et_2NCH{=}CH_2$.[30] The β-vinyl proton of the enamine is upfield shifted due to the shielding from n–π-electron interaction,[31,32] whereas the α-vinyl proton is less shielded than the β-vinyl proton and, in addition, substitution of an electronegative nitrogen at the α-position also results in α-proton deshielding, which gives rise to the downfield-shifted NMR signal.[33,34] The proton resonances at 1.37 (doublet, 3 H) and 9.11 ppm (quartet, 1 H) in benzene are assigned to acetaldehyde, which has been observed as a photoproduct in a similar system.[35] Diethylamine is also detected as a product. The latter compounds are accounted for most simply by hydrolysis of iminium ion, $Et_2N^+{=}CHCH_3$, which (vide infra) is intermediate en route to the enamine. The overall reaction between **1** and Et_3N is thus given by eq 4.

$$2Q + Et_3N \xrightarrow{h\nu} 2QH^\bullet + Et_2NCH{=}CH_2 \qquad (4)$$

The weak fluoresence of **1** in benzene appears to be slightly quenched upon addition of 0.05–0.1 M Et_3N; however, attempts to monitor fluorescence quenching are complicated by the efficient generation of a new fluorescing species (at 493 nm) which overlaps and rapidly dominates the weak fluorescence of **1** (Figure 3). The

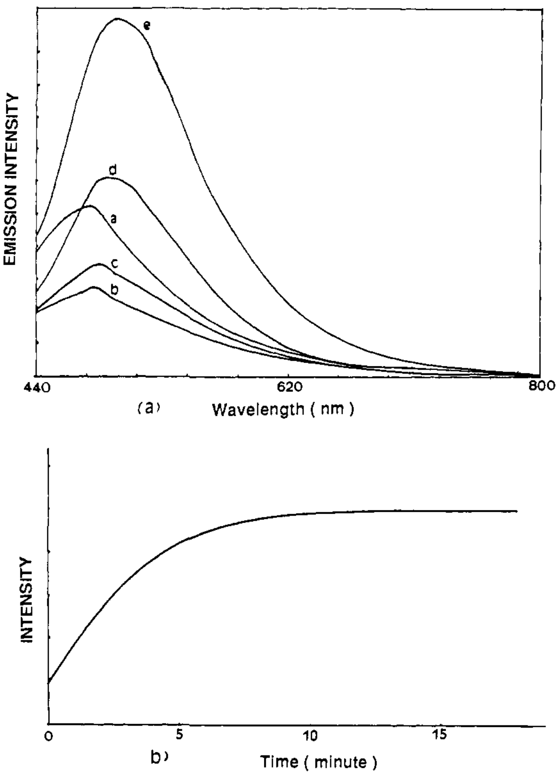


Figure 3. (a) Fluorescence of β-lapachone as a function of concentration of *erythro*-MDBOH (a, 0 M; b, 0.05 M; c, 0.1 M; d, 0.25 M; e, 0.4 M). (b) Fluorescence intensity (λ_{493}) of β-lapachone vs time during irradiation in the presence of *erythro*-MDBOH (0.1 M).

Table IV. Concentration Dependence of Photoreduction of β-Lapachone by Triethylamine

triethylamine concn, M	β-lapachone concn, M	ϕ_{red}[a]
0.02	5×10^{-4}	1.352
0.1	5×10^{-4}	1.460
0.4	5×10^{-4}	1.586
0.05	5×10^{-5}	0.278
0.05	1×10^{-4}	0.478
0.05	3×10^{-4}	0.832
0.05	5×10^{-4}	1.478

[a] Quantum yields were measured in benzene, and samples were vacuum degassed.

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Table V. Concentration Dependence of Photoreduction of β-Lapachone by **4** and **5**[a]

donor (concn, M)	β-lapachone concn, M	ϕ_{red}[b]
erythro-MDBOH (0.05)	5×10^{-5}	0.21
erythro-MDBOH (0.05)	1×10^{-4}	0.723
threo-MDBOH (0.05)	1×10^{-4}	0.235
erythro-MDBOH (0.05)	1.5×10^{-4}	0.820
erythro-MDBOH (0.05)	3×10^{-4}	1.240
erythro-MDBOH (0.05)	5×10^{-4}	1.454
threo-MDBOH (0.05)	5×10^{-4}	0.50
erythro-MDBOH (0.03)	5×10^{-4}	1.307

[a] **4** is *erythro*-MDBOH, and **5** is *threo*-MDBOH. [b] Samples were vacuum degassed, and quantum yields were measured in benzene.

Table VI. Solvent Effect on Reduction of β-Lapachone by **4**[a]

	benzene	CH_2Cl_2	CH_3COCH_3	CH_3CN	DMSO
ϕ_{red}[b]	0.723	0.563	0.463	0.380	0.103

[a] **4** is *erythro*-MDBOH. [b] [β-Lapachone] = 1×10^{-4} M, [**4**] = 0.05 M. Samples were vacuum degassed and quantum yields were measured in different solvents.

Table VII. Quantum Yield of Photoreduction of β-Lapachone by Benzyl Alcohol

benzyl alcohol concn, M	β-lapachone concn, M	ϕ_{red}[a]
1	2.5×10^{-5}	0.0194
1	5×10^{-5}	0.0271
1	1×10^{-4}	0.0715
1	3×10^{-4}	0.0902
1	5×10^{-4}	0.1242
$C_6H_5CH_2OH/C_6H_6 = 4/1$	5×10^{-4}	0.120

[a] Samples were vacuum degassed, and quantum yields were measured in benzene.

Table VIII. Isotope Effect on Photoreduction of β-Lapachone with Benzyl Alcohol

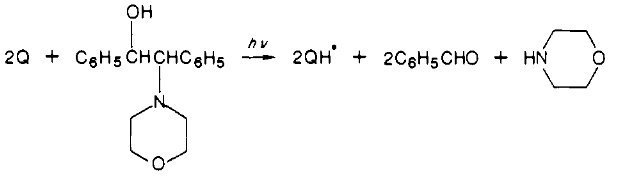
donor	ϕ_{red}[a]	isotope effect
$C_6H_5CH_2OH$ (1 M)	0.0902	$\phi_{C_6H_5CH_2OH}/\phi_{C_6H_5CD_2OH} = 3.84$
$C_6H_5CD_2OH$ (1 M)	0.0235	
$C_6H_5CH_2OD$ (1 M)	0.0827	$\phi_{C_6H_5CH_2OH}/\phi_{C_6H_5CH_2OD} = 1.09$

[a] [β-Lapachone] = 3×10^{-4} M; quantum yields were measured in benzene.

fluorescence intensity at 493 nm shows a reasonable correlation with the ESR signal assigned to **3** and appears to be due to this species.

The initial quantum efficiency of the photoreduction of **1** by Et_3N in degassed benzene shows a dependence upon both the concentration of quinone and amine (Table IV). The highest values obtained approach 1.6 and suggest a limit of 2 in terms of molecules of **1** reduced per photon. As has been discussed elsewhere, the products of photoreaction 4 are found to thermally return to starting material in dry, degassed benzene.[36] In contrast to the behavior of **1** upon photolysis with Et_3N, irradiation of **1** with the tertiary amine triethylenediamine (DABCO) leads to very little photoreduction to **3** (Table III). Although DABCO weakly quenches the fluorescence of **1**, only a faint ESR signal is observed during steady photolysis and no appearance of the "new" fluorescence at 493 nm is detected. Moreover, the ESR signal thus obtained during photolysis of **1** with DABCO was found in the same spectral width (80 G) where the ESR spectrum of radical cation of DABCO was located.[37,47] No fine structure, however, has been resolved at room temperature. Since the cation radical of DABCO shows a much wider ESR spectrum, which falls in the same region where that of **3** appears, it is possible that the signal is a superposition of the two species. This ESR spectrum is only observed during the photolysis and, in contrast to that observed with **1** and Et_3N, it decays quickly when the photolysis is interrupted.

Photoreaction of β-Lapachone with β-Amino Alcohols. Erythro and threo isomers of 1,2-diphenyl-2-morpholinoethanol (**4** and **5**) (MDBOH) also undergo very clean and efficient photoreaction with **1** under irradiation in degassed solution to generate **3** as the chief product from the quinone. As was demonstrated earlier for several other acceptors, the photooxidation of these donors occurs concurrent with C–C cleavage to yield net two-electron oxidation products; the overall reaction in this case is given by eq 5.[38] Here



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again the ESR spectrum of **3** is observed immediately upon photolysis and it persists without decay as the sample is stored in the dark. In this case no thermal return of the photoproducts to starting material is observed upon standing in the dark. As has been observed with other electron acceptors, there is an overall higher quantum efficiency of reaction for diastereomer **4** over **5** when comparable solutions are irradiated (Table V). However for **1** the efficiencies for both processes are relatively high and the difference in reactivity is much smaller than that observed for acceptors giving low overall reactivity such as 9,10-dicyanoanthracene and 1,4-dicyanonaphthalene.[38] In agreement with earlier studies of the photooxidation of **4** with electron acceptors, the photolysis of **1** with **4** shows a strong decrease in quantum efficiency as the solvent polarity is increased from benzene to dimethyl sulfoxide (Table VI).[39]

Photoreduction of β-Lapachone by Alcohols. Irradiation of **1** in the presence of alcohols such as 2-propanol or benzyl alcohol leads to spectral changes very similar to those shown in Figure 1. Here again photolysis in freeze–pump–thaw vacuum degassed samples leads cleanly to a single set of photoproducts (isosbestic points at 296 and 366 nm and λ_{max} at 316 nm); when the reactions are followed in an ESR tube the same 5-line spectrum observed

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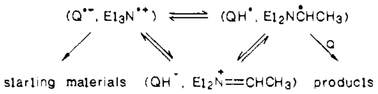
(39) The quantum yields measured in different solvents were done at a constant [**4**] = 0.05 M. Under these conditions deprotonation by $Q^{\bullet-}$ within the caged radical ion pair is probablly more likely than deprotonation by another amine, although at very high [**4**] a different situation could be attained.

(40) An alternative source of the second oxidation could be H-atom or electron transfer subsequent to the initial electron transer quenching:



Analogous net two-electron transfer processes have been observed for thioindigo with Et_3N.[26] Provided all three species lie reasonably close in energy (which appears likely), the ion pair of $QH^{\bullet-}$, $Et_2N^+{=}CHCH_3$, could be the relatively long lived state intercepted by Q as indicated by the concentration dependence of the quantum efficiency. A similar mechanism can also apply for the amino alcohols.

(41) The lifetime of triplet β-lapachone is measured by using argon-degassed benzene solution of β-lapachone, ca. 10^{-4} M. This value may be somewhat low due to a contribution from oxygen quenching.

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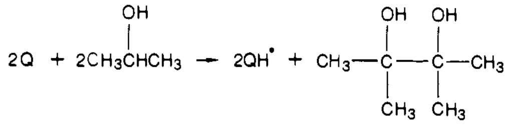
with **1**–Et_3N is detected and it persists indefinitely in the dark following photolysis. Exposure of irradiated solutions to air leads to rapid and quantitative regeneration of **1**. Similar behavior was observed for photolysis of oxalylindigo with 2-propanol. Thus, for both quinones it is clear that irradiation in the presence of these alcohols leads to accumulation of the semiquinone (eq 2) as the exclusive reaction. Products from oxidation of the alcohols were determined by NMR; for benzyl alcohol the major product was found to be benzaldehyde. The aldehyde proton was detected by NMR for both unlabeled benzyl alcohol and $C_6H_5CH_2OD$ but not from $C_6H_5CD_2OH$. Photolysis of 2-propanol in the presence of **1** leads to the formation of pinacol (0.93 ppm, singlet) and acetone (2.60 ppm, singlet), which were identified by comparison of NMR spectra with those of authentic samples in benzene. Thus for both alcohols the products are those characteristic of oxidation via the intermediate ketyl radicals and the overall reactions are summarized by eq 6 and 7.

$$2Q + C_6H_5CH_2OH \rightarrow 2QH^{\bullet} + C_6H_5CHO \quad (6)$$



$$2Q + 2CH_3\underset{}{\overset{OH}{C}}HCH_3 \rightarrow 2QH^{\bullet} + CH_3-\overset{OH}{\underset{CH_3}{C}}-\overset{OH}{\underset{CH_3}{C}}-CH_3 \quad (7)$$

The photoreaction between **1** and benzyl alcohol should be sensitive to concentrations on both **1** and the alcohol. A comparison of the reaction efficiency for 1 M benzyl alcohol in benzene and for 4:1 benzyl alcohol/benzene at the same concentration of β-lapachone indicates that a limiting quantum efficiency has been reached at 1 M alcohol. (Table VII). A strong variation of quantum efficiency with [**1**] is observed (Table VII) with a limiting efficiency (high [**1**], high [$C_6H_5CH_2OH$]) of ca. 0.12, much lower than the limiting reaction efficiencies between **1** and amines. The reaction between **1** and benzyl alcohol was also examined with deuterated alcohols; while a small reduction in efficiency was observed when $C_6H_5CH_2OD$ was compared with undeuteriated alcohol, a much more significant decrease in reactivity was observed when $C_6H_5CD_2OH$ was the reductant (Table VIII). The quantum efficiency for the photoreduction of **1** by 2-propanol was found to be much lower than that with benzyl alcohol.

Discussion

Mechanism of the Photoreduction of 1 with Amines. Comparison of the reduction potentials listed in Table II with oxidation potentials for the amines used in this study via the Weller equation indicates that the amines (Table IX) used should readily reduce singlet and triplet excited states of **1** by single-electron transfer. Although the weak fluorescence of **1** shows slight quenching by Et_3N, **4**, and DABCO, efficient photoreduction is observed at amine concentrations at which there is negligible fluorescence quenching. Thus it is reasonable that the triplet of **1** is the likely reactant in each case. This is also consistent with the generally high quantum efficiencies for photoreduction of **1** by the amines compared to cases where excited singlet states are the precursors to the initial electron-tranfser event.[30,38]

Table IX. Oxidation Potential of Electron Donors

electron donor	$E_p{}^a$ vs SCE
triethylamine	0.975
erythro-MDBOH	1.056
threo-MDBOH	1.212

[a] All the these amines gave irreversible oxidation peaks. E_p is the oxidation peak potential in volts.

The most reasonable reaction sequence for the photoreduction of **1** by Et_3N is given by eq 8–15, where the parentheses are

$$Q \xrightarrow{h\nu} Q^{1*} \xrightarrow{\gamma} Q^{3*} \quad (8)$$

$$Q^{3*} + Et_3N \rightarrow (Q^{\bullet -}, Et_3N^{\bullet +}) \quad (9)$$

$$Q^{3*} \rightarrow Q \quad (10)$$

$$(Q^{\bullet -}, Et_3N^{\bullet +}) \rightarrow Q + Et_3N \quad (11)$$

$$(Q^{\bullet -}, Et_3N^{\bullet +}) \rightarrow (QH^{\bullet}, Et_3N\dot{C}HCH_3) \quad (12)$$

$$(QH^{\bullet}, Et_2N\dot{C}HCH_3) \rightarrow Q + Et_3N \quad (13)$$

$$(QH^{\bullet}, Et_2N\dot{C}HCH_3) + Q \rightarrow (QH^{\bullet}, Et_2\overset{+}{N}{=}CHCH_3, Q^{\bullet -}) \quad (14)$$

$$(QH^{\bullet}, Et_2\overset{+}{N}{=}CHCH_3, Q^{\bullet -}) \rightarrow 2QH^{\bullet} + Et_2NCH{=}CH_2 \quad (15)$$

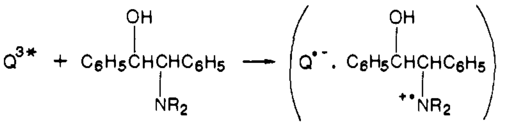
intended to denote "caged" species, which are not kinetically free.[40] The competition between return to ground-state starting materials (eq 13) and the second reduction of **1** (eq 14) is suggested by the strong dependence of the quantum efficiency on [1] (Table IV). Both of these steps should proceed at near diffusion-controlled rates, if bimolecular. Thus, if diffusion from the cage were to occur to give free $QH^{\bullet}$ and $Et_2N\dot{C}HCH_3$, the steady-state concentrations of $QH^{\bullet}$ (in early stages of the reaction) would be too low to permit the observed concentration dependence. The overall quantum efficiency is given by eq 16, where β is the efficiency

$$\phi_{QH^{\bullet}} = 2\gamma[k_9[Et_3N]/(k_9[Et_3N] + k_{10})]\,[k_{12}/(k_{11} + k_{12})]\,[\beta k_{14}[Q]/(k_{13} + k_{14}[Q])] \quad (16)$$

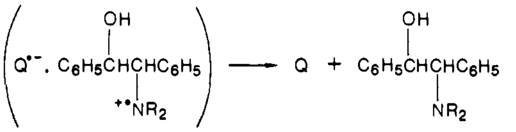
of product formation in eq 14 and it is assumed that reaction 15 occurs with unit efficiency. From eq 16, simpler relationships can be derived for the situations where either [Et_3N] or [Q] is varied with the other held constant. At constant [Q], a plot of $1/\phi$ vs $1/[Et_3N]$ should be linear with an intercept/slope = k_9/k_{10}, and intercept = $[(k_{13} + k_{14}[Q])/2\alpha\beta\gamma k_{14}[Q]]$, where $\alpha = k_{12}/(k_{11} + k_{12})$. The relatively small variation in ϕ vs [Et_3N] (Table IV) gives a reasonable double-reciprocal plot; if we assume a near diffusion controlled value for the quenching ($k_{14} \sim 5 \times 10^9$ M^{-1} s^{-1}), a value for the lifetime of the quenched intermediate ($\tau = 1/k_{10}$) of ca. 100–200 ns is obtained. This is in fair agreement with the ca. 500 ns lifetime estimated from time-resolved photoacoustic calorimetry.[41] At a constant [Et_3N] of 0.05 M the quantum efficiency for reduction of **1** shows a strong dependence on [Q]; a plot of $1/\phi$ vs $1/[Q]$ shows good linearity (correlation coefficient = 0.995) with a slope of 1.55×10^{-4} and an intercept of 0.526. Since quenching of triplet **1** should be >99% complete at this Et_3N concentration, the intercept value indicates that the product $\alpha\beta\gamma = 0.95$ or that the limiting quantum efficiency is 1.9. The intercept/slope = 3.4×10^3 M^{-1} and should reflect competition between reaction rate constants for eq 13 and 14.[40] Since reaction 14 is a moderately (~8 kcal/mol) exothermic electron-transfer process, it is reasonable that it occurs at close to a diffusion-controlled rate; assuming $k_{14} = 5 \times 10^9$ M^{-1} s^{-1} as above, a value of $k_{13} = 1.5 \times 10^6$ s^{-1} for the H-atom transfer is obtained, which seems to be a reasonable rate for such a process.[42] The overall high efficiencies observed for the **1**-Et_3N system are clearly attributable to relatively slow back electron transfer (k_{11}) and H-atom transfers (k_{13}) from the triplet ion radical and neutral radical pairs, respectively.

Amino alcohols **4** and **5** also give rise to efficient reduction of excited **1** and here again it is reasonable that reaction is initiated by triplet quenching. In this case the most reasonable mechanism involves eq 8 and 17–22.

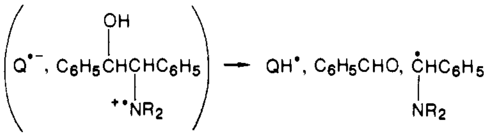
Here again our results suggest quenching is nearly complete where [**4**] = 0.05 M, but there is a clear dependence of ϕ on the concentration of quinone.[40] A plot of $1/\phi$ vs $1/[Q]$ for **4** gives a slope of 8.5×10^{-5} M^{-1} s^{-1} and an intercept of 0.568. The intercept indicates a limiting quantum efficiency, ϕ = 1.8, for **4** which is nearly as high as that for Et_3N. The intercept/slope = 6660 M^{-1} should reflect competition once again between a moderately exothermic electron transfer (eq 21) and a favorable H-atom transfer (eq 20). Assuming $k_{21} \sim 5 \times 10^9$ M^{-1} s^{-1}, we obtain $k_{20} = 7.5 \times 10^5$ s^{-1}, which is probably a reasonable value.[42] An interesting facet of the reaction between **1** and the amino alcohols is that reaction at very low [Q] should lead to a limiting "catalytic" role for the quinone in which an internal redox reaction (eq 23) is driven by the photolysis. Although this scheme predicts



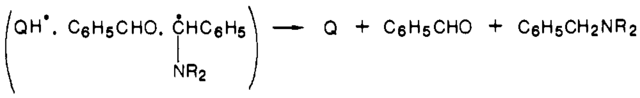
$$Q^{3*} + C_6H_5CH(OH)CH(NR_2)C_6H_5 \longrightarrow (Q^{\bullet-}.\ C_6H_5CH(OH)CH({}^{\bullet+}NR_2)C_6H_5) \quad (17)$$



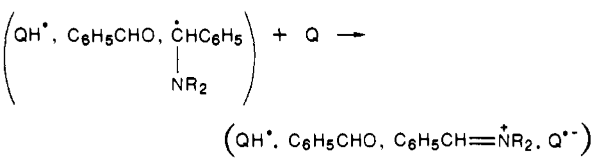
$$(Q^{\bullet-}.\ C_6H_5CH(OH)CH({}^{\bullet+}NR_2)C_6H_5) \longrightarrow Q + C_6H_5CH(OH)CH(NR_2)C_6H_5 \quad (18)$$



$$(Q^{\bullet-},\ C_6H_5CH(OH)CH({}^{\bullet+}NR_2)C_6H_5) \longrightarrow QH^{\bullet},\ C_6H_5CHO,\ \dot{C}H(NR_2)C_6H_5 \quad (19)$$

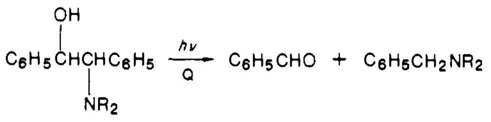


$$(QH^{\bullet}.\ C_6H_5CHO.\ \dot{C}H(NR_2)C_6H_5) \longrightarrow Q + C_6H_5CHO + C_6H_5CH_2NR_2 \quad (20)$$



$$(QH^{\bullet},\ C_6H_5CHO,\ \dot{C}H(NR_2)C_6H_5) + Q \longrightarrow (QH^{\bullet}.\ C_6H_5CHO,\ C_6H_5CH{=}\overset{+}{N}R_2.\ Q^{\bullet-}) \quad (21)$$

$$(QH^{\bullet},\ C_6H_5CHO.\ C_6H_5CH{=}\overset{+}{N}R_2.\ Q^{\bullet-}) \longrightarrow 2QH^{\bullet} + 2C_6H_5CHO + R_2NH \quad (22)$$



$$C_6H_5CH(OH)CH(NR_2)C_6H_5 \xrightarrow[Q]{h\nu} C_6H_5CHO + C_6H_5CH_2NR_2 \quad (23)$$

benzylmorpholine to be a product of the photolysis of **1** with **4** and **5**, we have not been able to detect it in experiments carried out with NMR detection. The lower reactivity of threo diastereomer **5** compared to erythro **4** follows the trend observed with other acceptors and is most readily attributed to a stereochemical preference for anticoplanar geometry in the fragmentation step (eq 19)[43,44] since all other steps would be expected to show little if any differences in rate for the two diastereomers. As pointed out earlier, there is a decrease in quantum efficiency with increase in solvent polarity (Table VI); although the precise origin of this effect remains uncertain, a reasonable possibility is that both quenching (eq 17) and reverse electron transfer (eq 18) can occur over distances greater than collisional. In nonpolar solvents close approach or contact is more likely so that fragmentation, which requires intimate contact between acceptor anion radical and donor cation radical, can compete with back electron transfer in what must be very close to a contact ion pair. In polar solvents electron transfer over a greater distance can produce a solvated or solvent-separated ion pair[45,46] such that back electron transfer can short-circuit the contact necessary for the fragmentation process.

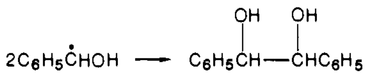
Mechanism of the Photoreduction of 1 with Alcohols. As pointed out above, the reaction of **1** with 2-propanol and benzyl alcohol gives analogous products (eq 6, 7) to those obtained with amines but with much lower overall efficiencies. The reaction with 2-propanol occurs with extremely low efficiencies compared to that with the amines; however, the reaction with benzyl alcohol occurs rapidly enough to be readily analyzed kinetically. The relative insensitivity of the photoreduction to change in benzyl alcohol concentration suggests that excited-state quenching is essentially complete at 1 M alcohol; a plot of $1/\phi$ vs $1/[Q]$ shows good linearity with a slope of 1.2×10^{-3} M^{-1} (correlation coefficient = 0.995) and an intercept of 6.2 (ϕ = 0.16). The likely mechanism for the photoreaction is given by eq 8 and 24–28. Although the pinacol (eq 28) was not detected for benzyl alcohol because of the interference of the signals from the starting material, it is a significant product with 2-propanol. The pronounced dependence of ϕ on [Q] could be attributed to a competition

$$Q^{3*} + C_6H_5CH_2OH \xrightarrow{\alpha k_{24}} (QH^{\bullet}.\ C_6H_5\dot{C}HOH) \quad (24)$$

$$(QH^{\bullet},\ C_6H_5\dot{C}HOH) \longrightarrow Q + C_6H_5CH_2OH \quad (25)$$

$$(QH^{\bullet},\ C_6H_5\dot{C}HOH) + Q \longrightarrow 2QH^{\bullet} + C_6H_5CHO \quad (26)$$

$$(QH^{\bullet}.\ C_6H_5\dot{C}HOH) \longrightarrow QH^{\bullet}. + C_6H_5\dot{C}HOH \quad (27)$$



$$2C_6H_5\dot{C}HOH \longrightarrow C_6H_5CH(OH){-}CH(OH)C_6H_5 \quad (28)$$

between in-cage H-atom transfer to regenerate starting material (eq 25) and interception of $C_6H_5\dot{C}HOH$ by a second ground-state quinone (eq 26). In this case the intercept/slope ratio of 5200 equals to the ratio k_{26}/k_{25}. Although reaction 26 shown above is a net H-atom transfer, it probably occurs by an electron transfer–proton transfer sequence since the electron-transfer step is likely to be slightly exothermic and probably much more rapid than an H-atom transfer. If this is the case, a value of 5200 is probably reasonable for the k_{26}/k_{25} ratio since reaction 25 cannot occur by a facile electron-transfer route.

The relatively low limiting quantum efficiency for the benzyl alcohol (and probably the 2-propanol reaction as well) mediated photoreduction of **1** is due to a low percentage of net H-atom abstraction in the quenching of triplet **1** by the alcohol.[48] The fraction of quenched triplets which lead to products, α, is estimated as 0.16. That the reaction proceeds via H-atom transfer is suggested by the marked decrease in quantum efficiency for $C_6H_5CD_2OH$; although a complete study of the reaction of **1** as a function of $[C_6H_5CD_2OH]$ was not carried out, the nearly 4-fold lowering of the quantum efficiency by deuterium substitution at the benzylic carbon suggests a lowered α may be the source of the reduced efficiency rather than a drastically lowered quenching (k_{24}) rate constant. Deuteriation at the OH in benzyl alcohol produces a small decrease, most consistent with a secondary isotope effect in the quenching vs H atom transfer branching of reaction 24. In summary, the results of this study demonstrate that excited quinones such as **1** are very reactive reagents toward potential electron and hydrogen atom donors. As a class of photoredox mediatiors they are especially attractive due to their relatively strong absorption at moderately long wavelengths. Since they react from triplet states the overall efficiency of net electron transfer can be reasonably high and even though the quinone undergoes preferential one-electron reduction to give $QH^{\bullet}$ as the stable or metastable product, the facile reduction of a second ground state quinone leads to overall two-electron reduction of the donor in most of the cases examined in this study. The photoreduction of β-lapachone contrasts strongly with the photoreduction of ketones, such as benzophenone, where quenching of triplets by alcohols leads to highly efficient H-atom transfer, however, since the quinone is not really a simple carbonyl chromophore, it is reasonable that the H-abstraction process may be more complex and overall less efficient. That interaction between the excited quinone may involve both the C–H and O–H of the alcohol is suggested by the observation of isotope effects by deuterium substitution in both positions. The strong dependence of reaction efficiencies on concentration of quinone in all three of the reactions investigated in detail highlight the importance of subsequent thermal reactions in the overall photoprocess and emphasizes the advantages of relatively soluble alkyl-substituted compounds such as β-lapachone.

Experimental Section

Materials. β-Lapachone was obtained by sulfuric acid treatment of the natural p-quinone lapachol[23,49] (from the Brazilian wood Bignoniaceae), which can also be made synthetically.[24] 1,2-Naphthoquinone and

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9,10-phenanthrenequinone were obtained from Aldrich and purified by vacuum sublimation. Benzene-d_6, CH_3CN-d_3, and D_2O (Aldrich, 99 + atom % D) were used without further purification.

Spectra-grade benzene (Aldrich) was purified by refluxing and distillation over sodium with benzophenone as indicator and was stored over sodium foil to eliminate water. Spectra-grade (Aldrich) acetonitrile was distilled from CaH_2 after refluxing and kept under 3A molecular sieves. Triethylamine (Aldrich) was distilled from potassium hydroxide prior to use. 2-propanol (spectra grade) was purified by distillation.

Erythro and threo isomers of 1,2-diphenyl-2-morpholinoethanol (MDBOH) were prepared from the reaction of morpholine with *trans*- and *cis*-stilbene epoxides, which were synthesized via epoxidation of *trans*- and *cis*-stilbene with *m*-chloroperbenzoic acid (MCPBA, Aldrich).[50] The crude products were recrystallized from 99% ethanol five times; their purity was further established by FT NMR. *erythro*-MDBOH mp 120–122 °C, *threo*-MDBOH mp 146–148 °C.

Dideuteriophenylcarbinol ($C_6H_5CD_2OH$) was prepared by reduction of ethyl benzoate with $LiAlD_4$. $LiAlD_4$ (2 g, 47.6 mmol; Aldrich, 98% D, used as received) was poured into 200 mL of dried diethyl ether (distilled from $LiAlH_4$) quickly. The solution was cooled down in an ice bath, and 20 g (133 mmol) of ethyl benzoate (Aldrich) was then injected slowly into the cooled solution. The reaction was kept in an ice bath with vigorous stirring (0.5 h), stirred at room temperature for 2 h, and finally refluxed for 0.5 h. This whole process was carried out under a N_2 atmosphere to avoid moisture. Upon cooling, 10 mL of a 10% NaOH solution was added to the ethereal solution followed by 20 mL of water to quench the excess $LiAlD_4$. The solution was filtered to remove lithium and aluminum hydroxides, dried over Na_2SO_4, and concentrated on a rotary evaporator. The crude product was purified by column chromatography (fresh silica gel with 10% ethyl acetate/hexanes as eluant). $C_6H_5CD_2OH$ (7.5 g) was obtained, with a yield of 60%. The purity of the sample was checked by FT NMR and the spectra showed >99% deuteriation at the α-position.

Benzyl alcohol-*d* ($C_6H_5CH_2OD$) was prepared by repeated washing of benzyl alcohol with excess D_2O. Benzyl alcohol (10 g; Aldrich, 99+%) was dissolved in 100 mL of dried benzene. D_2O (5 g) was added, and the solution was purged with N_2 for 10 min and stirred overnight under a N_2 atmosphere. The benzene/D_2O azeotrope was removed by distillation; afterward the remaining solution was treated with another 100 mL of dried benzene and 5 g of D_2O. The same cycle was repeated. All solvents, at the end, were evaporated under vacuum. The product (7 g) was obtained, which was checked by FT NMR, and it showed >95% deuteriation of the hydroxyl.

Photolyses and Product Analyses. The solutions were irradiated with either a 200-W Hg lamp or a Hanovia 450-W medium-pressure Hg lamp with a combination of Corning glass filters: a cutoff filter (3–73) and a band-pass filter (7–59) were used to isolate the 420-nm band for selective excitation of β-lapachone. Analysis of the photoproduct from the samples containing β-lapachone and various donors is complicated by the fact that the products are air sensitive. As a consequence, experiments were carried out under vacuum. All samples were degassed on a vacuum line through six to eight freeze–pump–thaw cycles in a round-bottom flask with an NMR tube as a side arm and sealed at $<3 \times 10^{-6}$ Torr with a torch; subsequently, the solution was transferred into the NMR tube and sealed. The whole process was carried out in a darkroom under a dim red light. The irradiation was performed in the NMR tube. The progress of photoreaction was monitored by taking NMR spectra periodically (300-MHz FT NMR; GE, Oxford Instrument). The photoproducts were identified by comparing their NMR and absorbance spectra with those of corresponding authentic samples, which were either synthesized or obtained commercially, and the detailed information has been provided in the Results section. Quantitative measurements were achieved by inserting an internal standard, in this case, methylcyclohexane. Parallel experiments were carried out by fusing a Pyrex test tube or cuvette onto the reservoir cell to allow for spectrophotometric monitoring of absorption or emission change of the solutions during photolysis.

Quantum yields were obtained by irradiating vacuum-degassed samples containing various concentrations of donor and β-lapachone in different solvents. The incident light intensities were measured with potassium ferrioxalate salt as actinometer.[51] Absorption spectra were recorded on a Hewlett-Packard 8451A spectrometer.

Kinetics and Product Measurement. Isotope experiments were performed with benzyl alcohol and its deuteriated derivatives ($C_6H_5CH_2OD$ and $C_6H_5CD_2OH$). The samples were vacuum degassed and irradiated with a 200-W Hg lamp with Corning glass filters (3–73, 7–59). The photoreactions were monitored by absorption and NMR spectra.

Fluorescence experiments were carried out with vacuum-degassed samples of 1×10^{-4} M β-lapachone with various concentrations of donors. Both wavelength-dependent fluorescence and time-dependent fluorescence were recorded on a SPEX Fluorolog fluorimeter.

Calorimetric measurements were obtained by photoacoustic techniques. A benzene solution of 1×10^{-4} M β-lapachone was argon degassed and photoexcited at 405 nm (PRA nitrogen laser) at room temperature. Photoacoustic signals were detected by a PZT transducer (Panametrics, Model 5657), digitized (LeCroy 9400 oscilloscope), and recorded by a computer. The calibration waves were obtained from the photoexcitation of ferrocene. The optical densities of the calibration compound and sample were adjusted to be within 2% of one another in order to avoid a concentration gradient of the heat-producing transient. The acoustic wave is then analyzed by a deconvolution program. The linear relationship between heat deposition and photoacoustic amplitude has been discussed elsewhere.[52-54]

The apparatus for electrochemical experiments has been described previously.[26a] For cyclic-voltammetry measurements, the reference electrode was $Ag/AgNO_3$ with a platinum wire as the counter electrode. The working electrode was a Teflon-shrouded platinum disk. Tetrabutylammonium tetrafluoroborate (0.1 M) was used as the supporting electrolyte. Typically, the substrate concentration is 0.005–0.01 M in dried acetonitrile, solutions were argon degassed for 20 min prior to the measurement.

The ESR spectra were taken with a Bruker spectrometer. The solutions for investigation were placed in a 2-mm diameter ESR tube and vacuum degassed through five freeze–pump–thaw cycles. The cell was then introduced into the cavity of a spectrometer equipped with accessories for variable-temperature control, magnetic field calibration, and frequency measurements. The samples were irradiated in the cavity with a high-pressure Hg lamp with Corning glass filters (3–73, 7–59). The spectra were recorded both during irradiation and after irradiation at various time intervals and in different solvents (benzene, CH_2Cl_2, 2-propanol).

Acknowledgment. We are grateful to the U.S. Department of Energy (Grant No. DE-FG02-86ER13504) for support of this research. X. Ci is grateful for a Messersmith Fellowship at the University of Rochester. The collaborations between the Universities of Rochester and Rio de Janeiro were made possible by support from the U.S. National Science Foundation and by the FINEP and the C.N.P.q. in Brazil. We thank Dr. Raymond Eachus, Dr. Myra Olm, and the Eastman Kodak Co. for assistance with techniques and instrumentation in carrying out the electron spin resonance experiments and Professor J. L. Goodman for assistance in the photoacoustic calorimetric studies.

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