

# Photoinduced Hydrogen Abstraction from Phenols by Aromatic Ketones. A New Mechanism for Hydrogen Abstraction by Carbonyl $n,\pi^*$ and $\pi,\pi^*$ Triplets

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**Abstract:** Nanosecond laser flash photolysis studies have been carried out of the kinetics of inter- and intramolecular phenolic hydrogen abstraction by alkoxyacetophenone, 5-alkoxyindanone, and 4-alkoxybenzophenone triplets in acetonitrile and benzene solution. Information on the geometric requirements for abstraction by carbonyl  $n,\pi^*$  and  $\pi,\pi^*$  triplets is derived from the results for a series of ketones which contain a *para*-phenolic moiety attached via a *para*-oxyethyl linkage. For all of these compounds, the deuterium kinetic isotope effect on the triplet lifetime in acetonitrile solution indicates that triplet decay is determined by the rate of intramolecular abstraction of the remote phenolic hydrogen, which yields the corresponding phenoxyl–hemipinacol biradical. The biradicals have also been detected, and are about an order of magnitude longer-lived than the triplet in each case. For three of the compounds, the rates of the intramolecular process follow the same trend as that observed in the rates of bimolecular quenching of the parent methoxy-substituted ketones by *p*-cresol. Deviation from this trend is observed for the alkoxyindanone derivative, where an in-plane approach of the phenolic hydrogen to the carbonyl  $n$ -orbital is not possible. The trends in the rate constants for bimolecular quenching of a series of substituted benzophenones by *p*-cresol indicate that for  $n,\pi^*$  triplet abstractions, the quenching mechanism is different for electron donor-substituted and electron acceptor-substituted ketones. For  $\pi,\pi^*$  triplets and donor-substituted ( $n,\pi^*$  triplet) benzophenones, abstraction is proposed to occur by a mechanism involving the intermediacy of a hydrogen-bonded exciplex, which yields the corresponding radicals by sequential electron- and proton-transfer. The rate constant for quenching by this mechanism thus depends mainly on the basicity of the ketone triplet state and the oxidation potential of the phenol.

## Introduction

Hydrogen abstraction is the most thoroughly studied photochemical reaction of aromatic ketones.<sup>1</sup> The process occurs by a variety of mechanisms depending (primarily) on the identity of the hydrogen donor, ranging from “pure” alkoxy-radical-like abstractions (as with alkanes<sup>2,3</sup>) to one initiated by full electron transfer to the excited carbonyl compound from the hydrogen donor (as with amines<sup>4–6</sup>). Abstraction of benzylic hydrogens occurs by a mechanism which spans both extremes, but is generally explainable in terms of the initial formation of a triplet exciplex in which the benzylic C–H bond is activated by charge transfer from the arene to the ketone.<sup>7</sup>

It is well-known that for aliphatic or benzylic hydrogen abstractions, ketones with lowest  $\pi,\pi^*$  triplet states are much less reactive than those with lowest  $n,\pi^*$  triplet states, and it is accepted that the former react predominantly via the higher energy  $n,\pi^*$  state, populated thermally from below.<sup>1,8</sup> Accordingly, the Arrhenius activation energies for abstractions of this type correspond to the energy difference between the  $\pi,\pi^*$  and  $n,\pi^*$  triplet states.<sup>9,10</sup> The differences in the reactivity of  $n,\pi^*$  and  $\pi,\pi^*$  triplet ketones toward bimolecular hydrogen abstrac-

tion are most aptly exemplified with the cases of benzophenone (lowest  $n,\pi^*$  triplet) and 4-methoxyacetophenone (lowest  $\pi,\pi^*$  triplet, with the  $n,\pi^*$  state ca. 3 kcal/mol higher in energy);<sup>8</sup> both ketones abstract hydrogen from xylene at rates about ten times higher than from cyclopentane, but benzophenone exhibits roughly hundred-fold higher reactivity than 4-methoxyacetophenone toward the two hydrogen donors.<sup>7,11</sup> Similar trends hold for intramolecular abstractions, as exemplified by the Norrish/Yang Type II photoreactivity of valerophenone and the 4-methoxy derivative.<sup>8</sup>

It has long been known that aromatic ketones abstract hydrogen from phenols at rates that are even faster than those from substituted toluenes.<sup>12</sup> While this might be expected on the basis of the fact that phenol has both a lower bond dissociation energy and lower oxidation potential than toluene (and the expectation that charge-transfer interactions should be correspondingly more pronounced), the characteristics of the process are clearly fundamentally different for the two hydrogen donors. With benzophenone, phenolic hydrogen abstraction occurs with rates 2–3 orders of magnitude faster than those for benzylic hydrogen abstraction, and is significantly faster in nonpolar solvents than in polar solvents. More interestingly, the reaction is *faster* for *p*-methoxypropiofenone than for benzophenone, and the deuterium kinetic isotope effect on the reaction (which indicates that hydrogen abstraction is the rate

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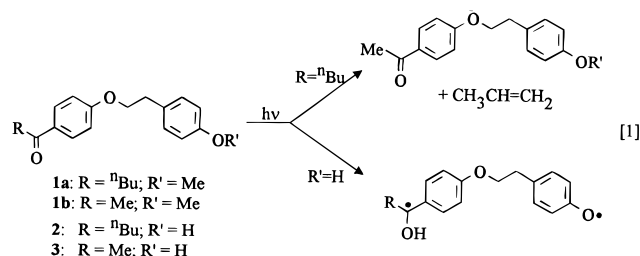
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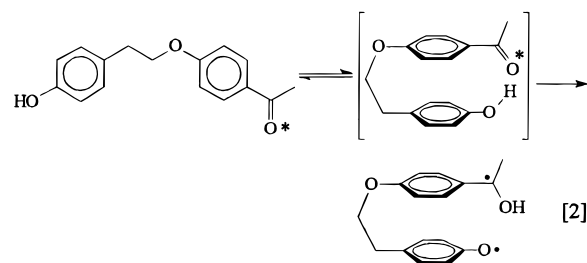
determining step in the process) is *higher* for the more reactive ketone.<sup>12</sup> From a study of the variation in quenching rates of benzophenone and 4-methoxypropiophenone triplets with substitution on phenol, it was concluded that the reaction exhibits substantial charge-transfer characteristics, with the ketone acting as electron-acceptor and the phenol as electron-donor.<sup>12</sup> This statement begs a comparison to abstractions from substituted toluenes, but thermodynamic considerations (*vide infra*) indicate that the exciplex mechanism proposed in the latter case cannot easily explain the unusually high reactivity of lowest  $\pi,\pi^*$  triplet ketones toward hydrogen abstraction from phenols, and neither can an electron-/proton-transfer mechanism analogous to that involved in photoreductions by amines.<sup>4,6</sup>

Some years ago, we reported a study of *intramolecular* phenolic hydrogen abstraction in the oxyethyl-linked phenolic ketones **2** and **3** (see eq 1).<sup>13</sup> Model compounds, in which the



phenolic hydrogen is replaced by a methyl group (**1a,b**), exhibit photochemistry which is typical of the *p*-alkoxybenzoyl chromophore in the absence of phenols. Thus, compound **1a** undergoes Norrish II cleavage to yield **1b** with a quantum yield ( $\Phi = 0.13 \pm 0.03$ ) similar to that of the Norrish II cleavage of *p*-methoxyvalerophenone,<sup>8</sup> while **1b** exhibits a triplet-triplet absorption spectrum similar to that of *p*-methoxyacetophenone ( $\lambda_{\text{max}} = 385 \text{ nm}^{14}$ ) and has a triplet lifetime of 2.6  $\mu\text{s}$  in deoxygenated acetonitrile solution at room temperature. The latter is significantly shorter than that of *p*-methoxyacetophenone under the same conditions however, suggesting that interactions between the carbonyl triplet and the remote *p*-alkoxyphenyl moiety enhance triplet decay to a minor extent in these compounds.

In the cases of **2** and **3**, the presence of the phenolic hydrogen has distinct effects on the photochemistry of the remote carbonyl group. Compound **2** exhibits substantially lower photoreactivity than **1a**; in fact, Norrish Type II cleavage is undetectable. Compound **3** exhibits a triplet-triplet absorption spectrum similar to that of **1b**, but the triplet is over two orders of magnitude shorter-lived. The lower triplet reactivity of **2** and short triplet lifetime of **3** were attributed to facile excited state deactivation by intramolecular abstraction of the remote phenolic hydrogen, leading to the formation of the phenoxy-hemipinacol biradical shown in eq 1. The biradical (R = CH<sub>3</sub>) could be detected directly by nanosecond laser flash photolysis techniques, and exhibits a lifetime of ca. 120 ns in acetonitrile solution at room temperature. The observation of a deuterium kinetic isotope effect ( $k_{\text{H}}/k_{\text{D}} = 1.8$ ) on the triplet decay rate of **3** in H(D)<sub>2</sub>O-saturated benzene solution is consistent with phenolic hydrogen abstraction being the rate determining process leading to deactivation of the triplet state, suggesting that in fluid solution, the conformational motions required for the molecule to achieve an appropriate geometry for intramolecular hydrogen abstraction (eq 2) occur over a somewhat faster time



scale than the actual abstraction process. Indeed, dissolution or inclusion of **3** in organized media such as liquid crystals<sup>15</sup> or cyclodextrins<sup>16</sup> results in substantial increases in the triplet lifetime, presumably owing to the restrictive effects of these media on the conformational mobility of the molecule.

The geometry for intramolecular hydrogen transfer in **3** is one in which potential charge-transfer interactions between the phenol and benzoyl  $\pi$ -systems are maximized. Based on Wagner's extensive work on ketone triplet abstractions from substituted toluenes, particularly those involving  $\pi,\pi^*$  ketone triplets,<sup>7</sup> this would clearly be expected to facilitate hydrogen abstraction by a similar, exciplex-mediated mechanism. It occurred to us that significant mechanistic insight into the reaction might be gained by determining how ketones with lowest  $n,\pi^*$  triplet states respond to structural constraints of this type, as well as what effects might result if the carbonyl *n*-orbitals were prevented from achieving good overlap with the phenolic hydrogen. Such factors could be relatively straightforward to investigate, given the inherent versatility of our synthetic approach to **3**.<sup>13</sup>

In this paper, we report the photochemistry of three new compounds which are related to **3**, but in which the photoreactive ketone is a 4-alkoxybenzophenone, 3,4-dialkoxyacetophenone, or 5-alkoxyindanone moiety. These compounds (**4–6**) were chosen in order to investigate the kinetics of phenolic hydrogen abstraction by  $\pi,\pi^*$  (**4** and **5**) and  $n,\pi^*$  (**6**) carbonyl triplets, under conditions where the relative geometry of the reacting moieties is fairly precisely controlled. The characteristics of the lowest triplet states of all three compounds have been studied in detail using nanosecond laser flash photolysis techniques and low-temperature phosphorescence emission spectroscopy. For comparative purposes, the non-phenolic methoxy analogs of **5** and **6** (**7** and **8**, respectively) have also been prepared and their triplet states characterized. Also, bimolecular rate constants for quenching of the triplet states of 4-methoxyacetophenone (**9**), 3,4-dimethoxyacetophenone (acetoveratrone, **10**), 5-methoxyindanone (**11**), and a series of substituted benzophenones (**12**) by *p*-cresol have been determined in acetonitrile solution.

The results can be interpreted in terms of a model in which the dominant rate-determining factor in phenolic hydrogen abstractions by relatively electron-rich ketones is the basicity of the lowest carbonyl triplet, which is highest in ketones with lowest triplet states of substantial  $\pi,\pi^*$  character.

## Results

Compounds **4–6** were synthesized by the general route shown in eq 3, by nucleophilic substitution of *p*-(trimethylsilyloxy)phenethyl bromide with the appropriate *p*-(hydroxyphenyl)ketone. Hydrolysis of the trimethylsilyl ether occurs during the second step, presumably during the aqueous workup. Com-

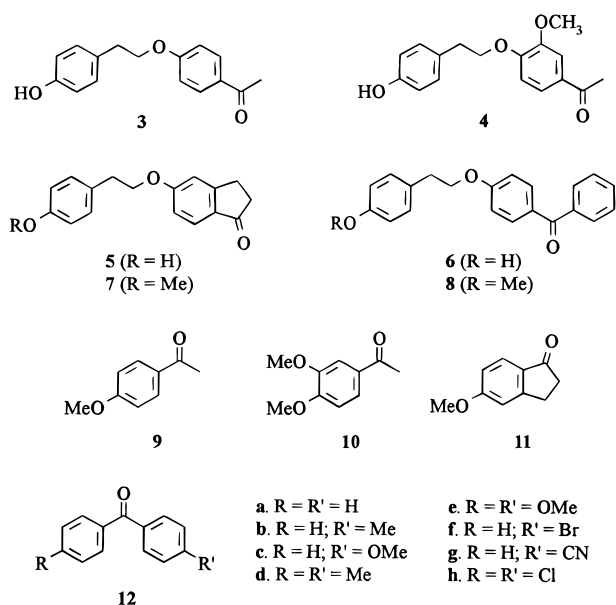
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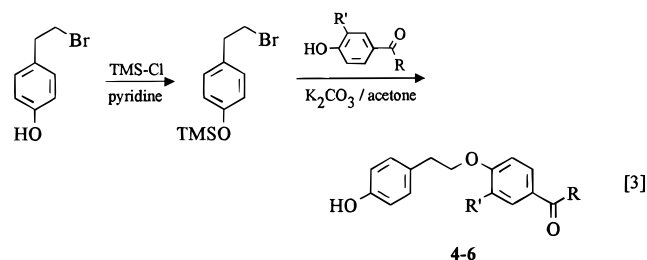
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Chart 1



Compounds **7** and **8** were prepared in analogous fashion from *p*-methoxyphenethyl bromide and 5-hydroxyindanone and 4-hydroxybenzophenone, respectively. The structures of **4–8** were assigned on the basis of their  $^1\text{H}$  and  $^{13}\text{C}$  NMR, infrared, and mass spectra.



The ultraviolet absorption spectra of **4–8** in acetonitrile solution are essentially identical to those of the simple methoxy-substituted ketones **10**, **11**, and **12c** in the same solvent. Thus, no indication of complexation between the carbonyl group and the remote phenolic moiety is evident from the static UV absorption spectra. Additionally, the infrared spectra of **4–6** in carbon tetrachloride solution exhibit absorptions in the 3300–3600- $\text{cm}^{-1}$  region characteristic of free phenols;<sup>17</sup> the spectra contain no indications of hydrogen bonding,<sup>18</sup> except in samples of relatively high concentration where intermolecular H-bonding would be expected.

Phosphorescence emission spectra and phosphorescence lifetimes of **3–8** were recorded in 4:1 ethanol/methanol glasses at 77 K. These are characteristic of the particular benzoyl chromophore present in each case, as indicated by comparison to spectral and lifetime data for the corresponding methoxy ketones **9–12c**, which in turn agree reasonably well with published parameters where available.<sup>7,8,19</sup> As expected, the fine structure in the spectra of all compounds except the benzophenones (**6**, **8**, and **12c**) is poorly resolved, such that the 0–0 bands are identifiable only as inflections on the short-wavelength edges of the spectra. The triplet energies (estimated from the positions

of the 0–0 emission bands or the highest energy shoulders<sup>8</sup>) and lifetimes are 70.5  $\pm$  0.3 kcal/mol ( $\tau = 250 \pm 10$  ms) for **3**, 67.3  $\pm$  0.3 kcal/mol ( $\tau = 360 \pm 20$  ms) for **4**, 72.5  $\pm$  0.3 kcal/mol ( $\tau = 360 \pm 20$  ms) for **5** and **7**, and 68.6  $\pm$  0.3 kcal/mol ( $\tau = 8.5 \pm 0.6$  ms) for **6** and **8**. The phosphorescence decays of all six of the ketones fit acceptably to single-exponential decay kinetics; we could not detect the expected multiexponential decays for the acetophenone derivatives,<sup>8,20</sup> probably because the data were rather noisy (our emission spectrometer is ill-suited for measurement of phosphorescence lifetimes of this magnitude). The lowest triplet states of **3–5** and **7** are assigned a  $\pi, \pi^*$  configuration, while those of **6** and **8** are assigned the  $n, \pi^*$  configuration, on the basis of the phosphorescence lifetimes and the presence or absence of fine structure in the spectra.<sup>7</sup> The data indicate that as expected, the presence of the phenolic moiety in these compounds has no discernible effect on the configuration of the lowest triplet state, and no effect on the triplet lifetime in a solid matrix at low temperature.

Deoxygenated 0.0025 M solutions of **4–6** in acetonitrile were irradiated (300 nm) simultaneously, with periodic monitoring of the solutions by gas chromatography. Irradiation for extended periods of time results in inefficient destruction of ketone and the formation of several minor products of considerably higher molecular weight than the starting ketone in each case. The quantum yields for photolysis of **4–6** were estimated to be in the 0.001–0.01 range using the disappearance of **3** ( $\Phi = 0.006^{13}$ ) as an actinometer. Presumably, decomposition of these compounds is due to some relatively inefficient secondary reaction of the phenoxy–hemipinacol biradicals formed by intramolecular hydrogen abstraction, as concluded previously for **3**.<sup>13</sup>

Laser flash photolysis (LFP) experiments employed pulsed excimer lasers filled with  $\text{N}_2/\text{He}$  (337 nm, 4 mJ,  $\sim 6$  ns),  $\text{Xe}/\text{HCl}/\text{He}$  (308 nm, 55 mJ,  $\sim 12$  ns), or  $\text{Kr}/\text{F}_2/\text{He}$  (248 nm, 60 mJ,  $\sim 12$  ns) for excitation, and a microcomputer-controlled detection system.<sup>16</sup> Samples were dissolved in acetonitrile, acetonitrile containing 5%  $\text{H}_2\text{O}$  or  $\text{D}_2\text{O}$ , or benzene, at concentrations such that the absorbance at the excitation wavelength (3 or 7 mm path length) was 0.2–0.7, and were deoxygenated with a stream of nitrogen until constant transient lifetimes (*vide infra*) were obtained in each case. In cases where triplet lifetimes were in the microsecond range (**7** and **8**), neutral density filters were employed to reduce the laser intensity and avoid contributions to the lifetimes from triplet–triplet annihilation.

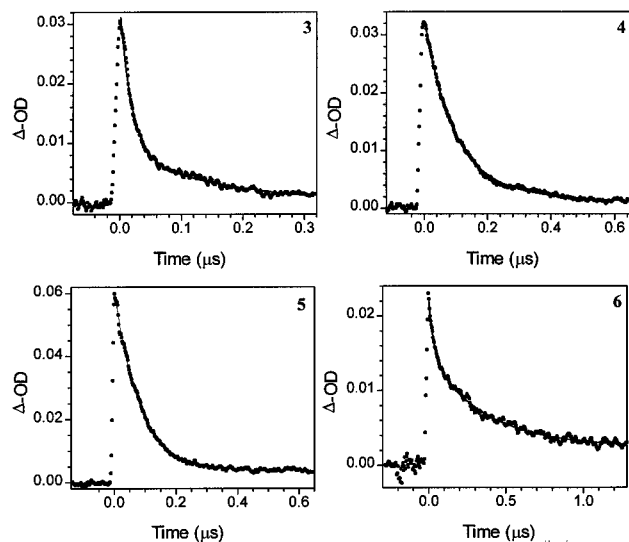
LFP of ketones **3–8** results in the observation of readily detectable transient absorptions in the 320–420 nm (**3–5**, **7**) or 400–700 nm (**6**, **8**) ranges. The non-phenolic ketones **7** and **8** exhibit relatively long-lived transient absorptions which decay with clean pseudo-first-order kinetics completely to the pre-pulse level. These were assigned to the corresponding triplet states on the basis of quenching by 1,3-cyclohexadiene ( $k_q \sim 1.1 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ ) and oxygen ( $k_q \sim 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ ), and comparisons of the time-resolved absorption spectra to the T–T absorption spectra of 5-methoxyindanone (**11**; *vide infra*) and 4-methoxybenzophenone (**12c**). Triplet lifetimes for these two compounds were found to be  $\tau_T = 0.28 \mu\text{s}$  for **7** and  $\tau_T = 5.0 \mu\text{s}$  for **8**, using rigorously deoxygenated solutions and substantially truncated laser intensities for recording of the decay traces. For **3–6**, the transient decays consist of two clearly distinct components, as reported previously for **3**.<sup>13</sup> Figure 1 shows typical transient decay traces for the four phenolic ketones in acetonitrile solution at 23  $^\circ\text{C}$ .

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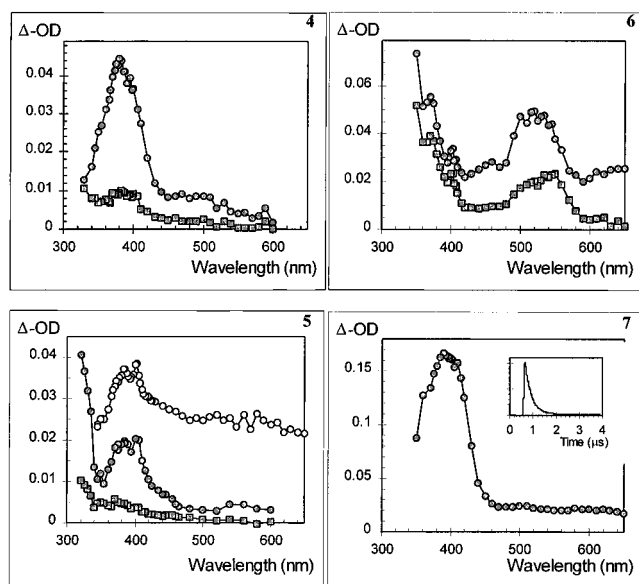
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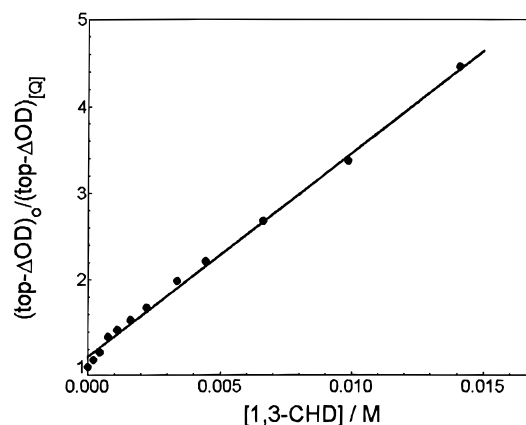
**Figure 1.** Transient decay traces from laser flash photolysis of deoxygenated, acetonitrile solutions of ketones 3–6 at 23 °C, at monitoring wavelengths of 385 (3–5) and 525 nm (6). Those for 3, 4, and 6 employed 248-nm excitation and  $\sim 2 \times 10^{-4}$  M solutions; that for 5 employed 308-nm excitation and a 0.004 M solution.



**Figure 2.** Transient absorption spectra recorded by 248-nm laser flash photolysis of deoxygenated,  $\sim 2 \times 10^{-4}$  M solutions of 4–7 at 23 °C, during the first  $\sim 10\%$  of the initial decay (●) and after the initial decay was complete (■). The additional, offset spectrum inserted in that for 5 was obtained from a deoxygenated acetonitrile solution of 5-methoxyindanone (0.006 M) and *p*-cresol (0.0011 M), recorded after the decay of the triplet was complete. The insert in the spectrum for 7 was recorded at a monitoring wavelength of 400 nm.

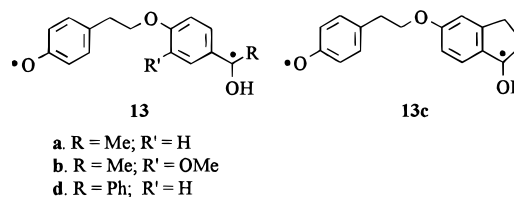
Transient absorption spectra were recorded in point-by-point fashion, over four time windows throughout the decays, using the 248-nm laser for excitation and ca.  $2 \times 10^{-4}$  M solutions of 3–8 in deoxygenated acetonitrile. The spectra recorded for 3 are similar to those reported previously.<sup>13</sup> Figure 2 shows the spectra obtained for 4–7 immediately after excitation and after the initial, short-lived decay was complete.

Addition of 1,3-cyclohexadiene (0.001 M) to the solutions of 3, 4, and 6 resulted in shortening of the lifetimes of the short-lived components and a decrease in the amount of long-lived component detectable. Saturation of the solutions with air had the same effect, and in addition led to a shortening of the lifetimes of the long-lived component of the decays. On the



**Figure 3.** Stern–Volmer plot of the quenching of the initial yield of the transient (top- $\Delta$ OD) from 308-nm NLFP of 5 in deoxygenated acetonitrile by 1,3-cyclohexadiene, monitored at 400 nm.

basis of these experiments, the short-lived decay components from LFP of 3, 4, and 6 are assigned to the carbonyl triplet states, while the long-lived decay components are assigned to the corresponding phenoxyl–hemipinacol biradicals 13a, 13b, and 13d, respectively.

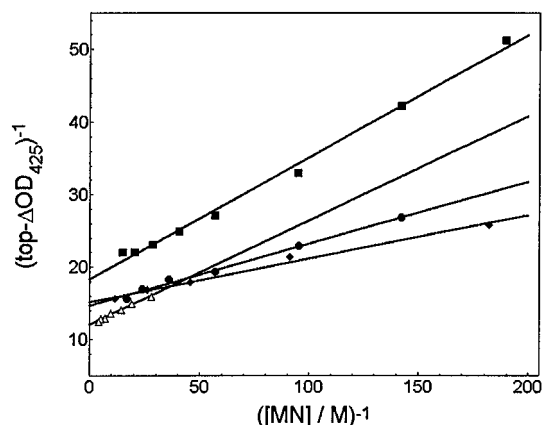


In the case of 5, the initial transient absorption decayed with a lifetime of  $\sim 90$  ns, to a minor residual absorption which appeared to be stable over several tens of microseconds. Addition of small amounts of 1,3-cyclohexadiene appeared to have no effect on either of these absorptions, but addition of larger quantities (using the 308-nm laser for excitation and a 0.0052 M solution of the ketone) led to reductions in the initial transient absorbance level (“top- $\Delta$ OD”) in proportion to the concentration of added diene, suggesting that the transient is a product of the triplet state of 5. A plot of  $(\text{top-}\Delta\text{OD})_0/(\text{top-}\Delta\text{OD})_{1[Q]}$  versus  $[Q]$  (eq 4), where  $(\text{top-}\Delta\text{OD})_0$  is the initial

$$(\text{top-}\Delta\text{OD})_0/(\text{top-}\Delta\text{OD})_{1[Q]} = 1 + k_q\tau_T[Q] \quad (4)$$

transient absorbance in the absence of diene and  $(\text{top-}\Delta\text{OD})_{1[Q]}$  is the transient absorbance in the presence of diene at concentration  $[Q]$ , is linear, as shown in Figure 3. The slope yields  $k_q\tau_T = 240 \pm 10 \text{ M}^{-1}$ , where  $k_q$  is the bimolecular rate constant for quenching of the triplet precursor, and  $\tau_T$  is the lifetime of the triplet in the absence of diene. On the basis of these results, the short-lived decay component in the trace shown in Figure 1 is assigned to biradical 13c. We are unable to assign the longer-lived residual absorptions observed in this case.

Lifetimes for the two decay components observed in the 248-nm LFP experiments with 3, 4, and 6 (Figure 1) were determined by curve-fitting to a two-exponential decay function, and are collected in Table 1. For 6, the lifetime of the short-lived (triplet) component obtained in this way ( $\tau_T = 19 \pm 3$  ns) agreed satisfactorily with that determined by single-exponential least-squares analysis of decay traces measured at 650 nm, where the longer-lived component does not absorb appreciably. Transient decays were also collected for 3, 4, and 6 at 4 °C, where the triplets are distinctly longer-lived than the excitation pulse width; triplet lifetimes recorded under these conditions



**Figure 4.** Double reciprocal plots for the quenching of **3** (■), **4** (◆), **5** (△), and **6** (●) by 1-methylnaphthalene in deoxygenated acetonitrile solution at 23 °C.

are also included in Table 1. The lifetimes of the long-lived decay components at 4 °C were increased by 20–50% compared to their values at room temperature.

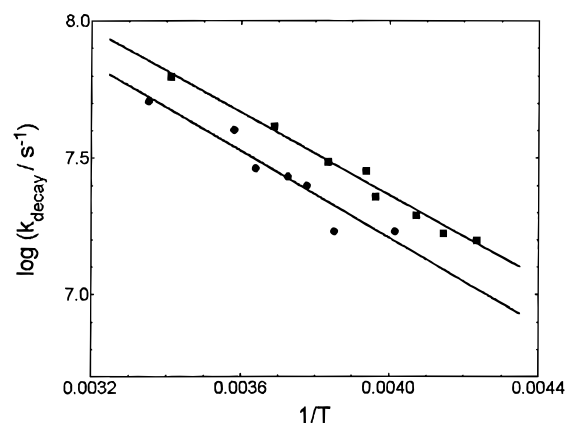
The above assignments and triplet lifetimes were verified using the 1-methylnaphthalene (MN) probe method,<sup>21,22</sup> and the 337-nm nitrogen laser for excitation of deoxygenated acetonitrile solutions of the ketones. Addition of MN to the solutions resulted in the “instantaneous” formation of the triplet state of the arene, characterized by its distinctive triplet–triplet absorption spectrum ( $\lambda_{\max} = 425$  nm), and in the cases of **3**, **4**, and **6**, reductions in the lifetime of the ketone triplet. For these three compounds, determination of the initial absorbance due to the MN triplet at 425-nm ( $\text{top-}\Delta\text{OD}_{425}$ ) as a function of [MN] was straightforward, and reciprocal plots of the data according to eq 5 were linear. In the case of **5**, determination of the initial

$$(\text{top-}\Delta\text{OD}_{425})^{-1} = (I_a \phi_{\text{isc}} / \epsilon_{425}) (1 + (k_q \tau_T)^{-1} [\text{MN}]^{-1}) \quad (5)$$

MN<sup>3</sup> absorbance was more difficult because of competing absorption due to the biradical (**13c**), and required extrapolation at the lower MN concentrations. Figure 4 shows examples of reciprocal plots for the four compounds, while Table 1 lists the  $\tau_T$  values obtained from the intercept/slope ratios, using a value of  $k_q = 8 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ , the average of several independent determinations with the model compounds **9–12c**.

A potential problem in the interpretation of the triplet lifetime data for **3–6** arises from the need to account for contributions from bimolecular hydrogen abstraction (self-quenching), rate constants for which can be approximated as those of quenching of the corresponding model compounds (**9–12c**) by *p*-cresol (*vide infra*). Only in the case of **5** was it necessary to employ solutions of concentration high enough for self-quenching to contribute more than ~5% to the measured values. For this compound, the data in Table 1 have thus been corrected accordingly.

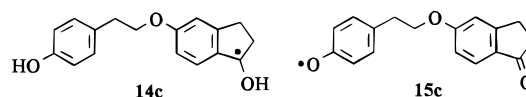
The temperature dependence of triplet decay was determined for **3** and **6** between 23 and –35 °C. Triplet lifetimes for **3** were determined by curve-fitting of decay traces recorded at 385 nm, while those for **6** were determined by least-squares analysis of the monoexponential decay traces recorded at 650 nm. Arrhenius plots are shown in Figure 5, and led to  $E_a = 3.8 \pm 0.3 \text{ kcal/mol}$ ,  $\log A = 10.7 \pm 0.3 \text{ s}^{-1}$  for **3**, and  $E_a = 3.5 \pm 0.3 \text{ kcal/mol}$ ,  $\log A = 10.2 \pm 0.3 \text{ s}^{-1}$  for **6**.



**Figure 5.** Arrhenius plots for triplet decay of **3** (■) and **6** (●) in deoxygenated acetonitrile solution. The decay rate constants were measured by direct detection (248 or 308-nm excitation,  $2 \times 10^{-4}$  M solutions) at 385 (**3**) or 650 nm (**6**).

Triplet lifetimes were determined in similar fashion (i.e., by direct detection with 248-nm excitation (**3**, **4**, and **6**), Stern–Volmer quenching with 1,3-cyclohexadiene with 308-nm excitation (**5**), and the MN-probe method with 337-nm excitation (**3**, **4**, and **6**)) in deoxygenated acetonitrile containing 5% water or deuterium oxide. The Stern–Volmer plots for quenching of the biradical absorption from **5** in acetonitrile containing 5% H<sub>2</sub>O or D<sub>2</sub>O were linear, affording slopes of  $k_q \tau_T = 117 \pm 10$  and  $98 \pm 10 \text{ M}^{-1}$ , respectively. Table 1 lists the  $\tau_T$  values obtained from these experiments.

The transient behavior observed for compound **5** varied with excitation wavelength, but this can be attributed to the variations in bulk ketone concentration which were necessary for excitation at the various wavelengths. Excitation with the 308-nm laser (ketone concentration of  $\sim 10^{-3}$  M) afforded similar results to those obtained with the 248-nm laser (and  $\sim 10^{-4}$  M solutions), but with a ~20% increase in the lifetime of the initial transient. Traces recorded with the 337-nm laser (ketone concentration  $\sim 10^{-2}$  M) contained a substantially longer-lived initial decay ( $\tau \sim 250$  ns) and a much larger residual absorbance, which decayed over several tens of microseconds. Transient spectra recorded at various time intervals after the laser pulse were all similar to that assigned to biradical **13c** (see Figure 2). We believe that the more complex decays observed under these conditions are largely due to the corresponding hemipinacol and phenoxy radicals (**14c** and **15c**, respectively), formed by bimolecular quenching of the triplet by hydrogen abstraction from ground-state ketone (i.e., self-quenching), in addition to biradical **13c**.



Triplet lifetimes were also determined in deoxygenated benzene solution using 308-nm excitation, and are also listed in Table 1. The transient decays followed similar forms to those recorded in acetonitrile solution, but the triplets were shorter-lived. In the case of **5**, the long-lived residual absorptions comprised ~30% of the initial transient absorbance, but were similarly unaffected by addition of diene. The triplet lifetimes of **3** and **6** were determined using the MN-probe method, while that for **5** was determined by Stern–Volmer quenching with 1,3-cyclohexadiene (using a value of  $k_q = 6 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$  for the quenching rate constant). The triplet state of **4** proved to be too short-lived to be measured reliably ( $\tau_T \leq 17$  ns), and

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**Table 1.** Lifetimes of Carbonyl Triplets in 4:1 Ethanol/Methanol at 77 K, in Acetonitrile (MeCN) at 23 and 4 °C, and in 5% H<sub>2</sub>O/MeCN, 5% D<sub>2</sub>O/MeCN, and Benzene at 23 °C and of 1,13-Phenoxy–Hemipinacol Biradicals (**13**) in MeCN at 23 °C<sup>a</sup>

compd	EtOH/MeOH 77 K; ms <sup>b</sup>	MeCN 23 °C; ns	MeCN 4 °C; ns	5% H <sub>2</sub> O/MeCN 23 °C; ns	5% D <sub>2</sub> O/MeCN 23 °C; ns	benzene 23 °C; ns	τ <sub>13</sub> (ns) (MeCN; 23 °C)
<b>3</b>	256	14 (15 <sup>c</sup> )	19	14 <sup>c</sup>	19 <sup>c</sup>	4 <sup>c</sup>	170
<b>4</b>	340	55	92	34 (31 <sup>c</sup> )	49 <sup>c</sup>	≤ 17 <sup>e</sup>	175
<b>5</b>	350	27 (22 <sup>d,f</sup> ) 14 (10 <sup>c,f</sup> )		15 (11 <sup>d,f</sup> )	17 (13 <sup>d,f</sup> )	23 (18 <sup>d,f</sup> )	90
<b>6</b>	8.4	19 (20 <sup>c</sup> )	35	17 <sup>c</sup>	19 <sup>c</sup>	≤ 14 <sup>e</sup> (8 <sup>c</sup> )	285

<sup>a</sup> Direct measurement by 248-nm LFP, using rigorously deoxygenated, 0.8–1.2 × 10<sup>-4</sup> M solutions, unless otherwise noted. Errors are ~10%. Self-quenching corrections have been applied where necessary, or are negligible under the conditions employed. <sup>b</sup> Phosphorescence lifetime. <sup>c</sup> Estimated from  $k_{qt}$ -values for 1-methylnaphthalene quenching, obtained by 337-nm LFP of rigorously deoxygenated, 0.01 (**3**), 8 × 10<sup>-4</sup> (**4**), 0.018 (**5**), or 0.006 (**6**) M solutions, and using  $k_q = 8 \times 10^9$  (MeCN) or 6 × 10<sup>9</sup> M<sup>-1</sup> s<sup>-1</sup> (benzene). Errors are ~10% except in the case of **5** (see text). <sup>d</sup> Estimated from  $k_q\tau_T$ -value for 1,3-cyclohexadiene quenching of biradical formation, obtained by 308-nm LFP of rigorously deoxygenated, 0.0052 M solutions, and using  $k_q = 1.1 \times 10^{10}$  M<sup>-1</sup> s<sup>-1</sup>. Errors are ~10%. <sup>e</sup> Direct measurement by 308-nm LFP. The decay of the triplet followed the laser pulse. <sup>f</sup> The raw value, before correction for self-quenching.

**Table 2.** Rate Constants for Bimolecular Quenching (in Units of 10<sup>9</sup> M<sup>-1</sup> s<sup>-1</sup>) of the Triplet States of Aromatic Ketones (**9–12**) by *p*-Cresol in Deoxygenated Acetonitrile Solution at 23.0 ± 0.5 °C<sup>a</sup>

ketone	$k_q/10^9$ M <sup>-1</sup> s <sup>-1</sup>
4-methoxyacetophenone ( <b>9</b> )	1.24 ± 0.03
acetoveratrone ( <b>10</b> )	0.80 ± 0.05
5-methoxyindanone ( <b>11</b> )	1.74 ± 0.13
benzophenone ( <b>12a</b> )	0.34 ± 0.03
4-methylbenzophenone ( <b>12b</b> )	0.58 ± 0.03
4-methoxybenzophenone ( <b>12c</b> )	1.17 ± 0.07
4,4'-dimethylbenzophenone ( <b>12d</b> )	1.08 ± 0.07
4,4'-dimethoxybenzophenone ( <b>12e</b> )	2.4 ± 0.2
4-bromobenzophenone ( <b>12f</b> )	0.86 ± 0.12
4-cyanobenzophenone ( <b>12g</b> )	3.9 ± 0.2
4,4'-dichlorobenzophenone ( <b>12h</b> )	2.1 ± 0.2

<sup>a</sup> Errors are given as twice the standard deviation of the least squares slope from analysis of  $k_{\text{decay}}$  vs [*p*-cresol] according to eq 6.

low solubility in benzene precluded estimation of its lifetime by the MN-probe method.

Absolute rate constants for bimolecular triplet quenching of **9–12** by *p*-cresol were determined in deoxygenated acetonitrile solution at 23 °C using the 337-nm laser for excitation, by monitoring the pseudo-first-order triplet decay rate ( $k_{\text{decay}}$ ) at 380 (**9–11**) or 525 nm (**12**) as a function of the concentration of added cresol. In each case, the addition of *p*-cresol resulted in a change in the form of the transient decay profile, from one which decayed cleanly to the pre-pulse level with pseudo-first-order kinetics in the absence of phenol, to one consisting of an initial, rapid pseudo-first-order (triplet) decay followed by a slower, second-order decay. The time-resolved absorption spectra of the latter are consistent with a superposition of spectra due to the *p*-cresyloxy and corresponding hemipinacol radicals, and are very similar to the spectra assigned to the biradicals from LFP of **3–6**. That of the radical pair from 5-methoxyindanone (**11**) and *p*-cresol is shown as an insert in Figure 2. Linear least-squares analysis of a plot of the triplet decay rate constants as a function of *p*-cresol concentration according to eq 6 afforded the quenching rate constants  $k_q$  listed in Table 2.

$$k_{\text{decay}} = k_o + k_q[\text{Q}] \quad (6)$$

Rate constants for quenching of the triplet states of **9–12c** by *p*-cresol were also determined in 5% aqueous acetonitrile solution. Those for **9** and **12c** were the same as those determined in dry acetonitrile, within experimental error, but values of  $k_q = (2.9 \pm 0.1) \times 10^8$  and  $(1.0 \pm 0.1) \times 10^9$  M<sup>-1</sup> s<sup>-1</sup> were obtained for **10** and **11**, respectively. Addition of water to deoxygenated acetonitrile solutions of the four ketones reduced the lifetime and initial top-ΔOD value of the triplet state of **11** markedly, but had no discernible effect on the triplet–triplet absorptions of the other three.

## Discussion

The transient spectroscopic behavior of **3** reported here is in excellent agreement with that reported previously;<sup>13</sup> in deoxygenated acetonitrile solution, the transient decays consist of two components assignable to the triplet state of the ketone ( $\tau = 14$  ns) and the corresponding phenoxy–hemipinacol biradical (**13a**;  $\tau = 162$  ns). The acetoveratrone-derived compound **4** and the alkoxybenzophenone **6** show analogous behavior, with the lifetimes of the short-lived (triplet) components mirroring the trend in the bimolecular rate constants for quenching of 4-methoxyacetophenone (**9**), acetoveratrone (**10**), and 4-methoxybenzophenone (**12c**) by *p*-cresol.

The triplet state assignment for these transients is based on the similarities between their UV absorption spectra and the triplet–triplet absorption spectra of **9**, **10**, and **12c**, respectively, and the results of 1,3-cyclohexadiene and 1-methylnaphthalene quenching experiments. The  $\tau_T$ -values extracted from (reciprocal) Stern–Volmer analyses of the 1-methylnaphthalene data are in reasonable agreement with those obtained by direct detection.

The assignment of the long-lived decay components from LFP of **3**, **4**, and **6** (and the short-lived one from **5**) to the corresponding phenoxy–hemipinacol biradicals (**13**) is made on the basis of the similarities of their UV absorption spectra to the summed spectra of the *p*-cresyloxy and corresponding hemipinacol monoradicals (as obtained from transient spectra recorded for mixtures of **9–11**, **12c**, and *p*-cresol), and the sensitivity of the lifetimes and initial yields to the presence of oxygen. Also, addition of 1,3-cyclohexadiene reduces the extrapolated initial yield of the transient but has little effect on the lifetime in all three cases, verifying that it is the product of a quenchable triplet. The main pathway for biradical decay would appear to be reversion to the starting phenolic ketone, as suggested previously for **13a**.<sup>13</sup> This is consistent with the extremely low quantum yields for photolysis of the three ketones, and the (related) fact that solutions of **3–6** could be subjected to literally hundreds of laser pulses without detectable change in the temporal characteristics or intensities of the transient absorptions.

The transient spectroscopic behavior of ketone **5** is significantly different from those observed for the other three compounds. In this case, the short-lived transient absorption is more reasonably assigned to biradical **13c** than to the triplet state of the molecule. This assignment is based on both the UV absorption spectrum (which is similar to the superposed spectra of the *p*-cresyloxy and 5-methoxyindanone–hemipinacol radicals, and lacks the intensity of the triplet–triplet absorption spectrum of the methoxy-substituted analog **7**) and the response of the transient to addition of triplet quenchers. Stern–Volmer quenching of the biradical absorption with 1,3-

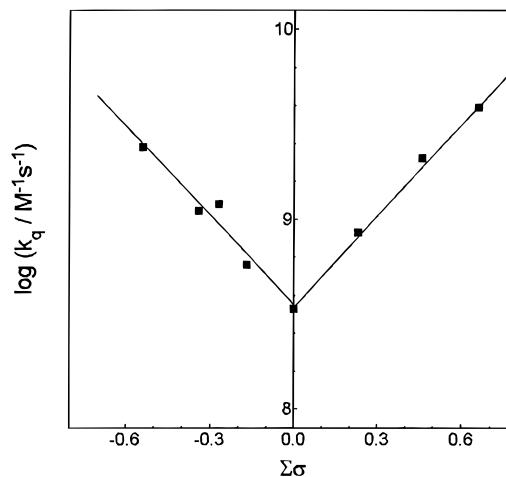
cyclohexadiene leads to a triplet lifetime of  $\tau_T = 27 \pm 4$  ns at 23 °C, after correction for self-quenching. This is a factor of only about three shorter than that of the biradical, and may partially explain why we are unable to resolve the triplet from the  $\sim 90$  ns biradical decay. The 1-methylnaphthalene quenching experiments are more difficult to analyze in this case because of overlap between the absorption spectra of **13c** and MN<sup>3</sup>; nevertheless, the triplet lifetime obtained ( $\tau_T = 14 \pm 6$  ns) is in reasonable agreement with the more precise value obtained from cyclohexadiene quenching.

The triplet lifetimes of **3–6** are all slightly longer in 5% D<sub>2</sub>O/MeCN than in 5% aqueous acetonitrile, leading to  $k_H/k_D$  values in the 1.1–1.6 range. The value found here for **3** in aqueous acetonitrile ( $k_H/k_D = 1.4$ ) is slightly lower than the value of 1.8 that was reported previously for this compound in wet benzene and attributed to a primary kinetic isotope effect.<sup>13</sup> The trend in the  $k_H/k_D$  values for **3** and **6** is similar to that for bimolecular quenching of benzophenone and *p*-methoxypropiofenone triplets by phenol in aqueous acetonitrile ( $k_H/k_D = 1.2$  and 3.9, respectively).<sup>12</sup> The trend in the KIE's for **3–5** (**4** > **3** > **5**) is the expected one considering the difference in the rates of bimolecular abstraction from *p*-cresol by the corresponding model compounds (**9**, **10**, and **11**) and the fact that all three of these compounds have lowest triplet states of similar ( $\pi, \pi^*$ ) configuration.

It has already been reported that the triplet lifetime of **3** is greater in hydrogen-bond accepting solvents compared to benzene,<sup>13</sup> and comparison of the triplet lifetimes of **4–6** in acetonitrile and benzene suggests that these three ketones behave in similar fashion to **3** in this respect as well. This effect is also evident in the (reported) rate constants for bimolecular phenolic hydrogen abstractions by benzophenone,<sup>12</sup> *p*-methoxypropiofenone,<sup>12</sup> and biacetyl<sup>23</sup> triplets, and attributed to a reduction in the concentration of free (reactive) phenol due to hydrogen bonding with the solvent.<sup>23</sup> Similar effects are observed on the rate constants for alkoxy radical abstractions from phenol.<sup>24–26</sup>

It is interesting that the triplet decay rates of **4** and **5** in acetonitrile are significantly higher in the presence of water, in spite of the fact that the bimolecular rate constants for triplet quenching of the corresponding model compounds (**10** and **11**) by *p*-cresol are lower in 5% aqueous acetonitrile than in the dry solvent. We are unable to suggest a totally satisfactory explanation for this; similar behavior is not observed for **3** and **6**, nor is it for bimolecular quenching of their model compounds (**9** and **12c**). It is possible that the lower rates of bimolecular quenching of **10** and **11** in the presence of water are due to the effects of triplet state hydrogen bonding (*vide infra*) with the cosolvent. However, similar effects would most likely be expected on the rate of the intramolecular process, unless water assists in the intramolecular hydrogen transfer by acting as a “bridge” between the phenolic hydrogen and the carbonyl oxygen. The possibility that addition of water causes solute aggregation, and shortened triplet lifetimes due to an increased contribution from self-quenching, can probably be ruled out by the failure of **3** and **6** to behave similarly.

**Bimolecular Phenolic Hydrogen Abstraction by  $n, \pi^*$  and  $\pi, \pi^*$  Triplet Ketones.** The rate constants for bimolecular abstraction from *p*-cresol by the substituted benzophenones



**Figure 6.** Plot of  $\log k_q$  versus Hammett substituent constants ( $\Sigma\sigma$ ),<sup>27</sup> for the quenching of substituted benzophenone triplets (**12a–f**) by *p*-cresol in deoxygenated acetonitrile solution at 23 °C.

**12a–f** (all lowest  $n, \pi^*$  triplets) are shown plotted against Hammett substituent constants<sup>27</sup> in Figure 6. The plot shows clear indications of a fundamental difference in mechanism for the quenching of donor- ( $\rho = -1.6 \pm 0.3$ ) and acceptor-substituted ( $\rho = 1.9 \pm 0.1$ ) benzophenones by the phenol. Benzophenone itself is quenched the slowest of the eight compounds studied, and clearly lies at the borderline of the two mechanisms.

The positive Hammett  $\rho$ -value observed for quenching of the acceptor-substituted benzophenones (**12f–h**) is similar to that reported by Wagner and co-workers for quenching of substituted benzophenone triplets by *p*-xylene in acetonitrile solution, although in that case, linear behavior is observed over the complete range of electron-donor and -acceptor substituents studied.<sup>7</sup> These data were rationalized in terms of a mechanism involving the initial formation of an “*n*-type” exciplex with substantial charge-transfer (ketone acceptor/arene donor) character, analogous to the mechanism proposed by Singer and co-workers for the (non-productive) quenching of benzophenone triplets by electron-rich benzenes.<sup>28</sup> The data for **12f–h** are consistent with this mechanism, and correspond with the negative Hammett  $\rho$  value reported by Scaiano and co-workers for quenching of benzophenone triplets by substituted phenols in benzene and aqueous acetonitrile.<sup>12</sup> The mechanism for quenching of these compounds by phenols can be expected to vary between those for toluenes (charge-transfer exciplex)<sup>7</sup> and anilines (full electron transfer followed by proton transfer),<sup>4,6</sup> depending on the reduction potential of the ketone. Indeed, the quenching of biacetyl triplets by substituted phenols and anilines shows many similar characteristics.<sup>29</sup> While further work is clearly necessary to more precisely define the quenching mechanism for electron-acceptor substituted benzophenones, we identify this as the “normal” mechanism for quenching of  $n, \pi^*$  ketone triplets by phenols, in that it exhibits similar characteristics to abstraction from substituted toluenes.

The trend observed for quenching of the donor-substituted benzophenones by *p*-cresol suggests that as quenching by the normal mechanism becomes slower, a second mechanism grows in importance and eventually “takes over” as substituent donor strength increases. The negative Hammett  $\rho$  value is consistent with a mechanism in which the dominant role of the ketone is

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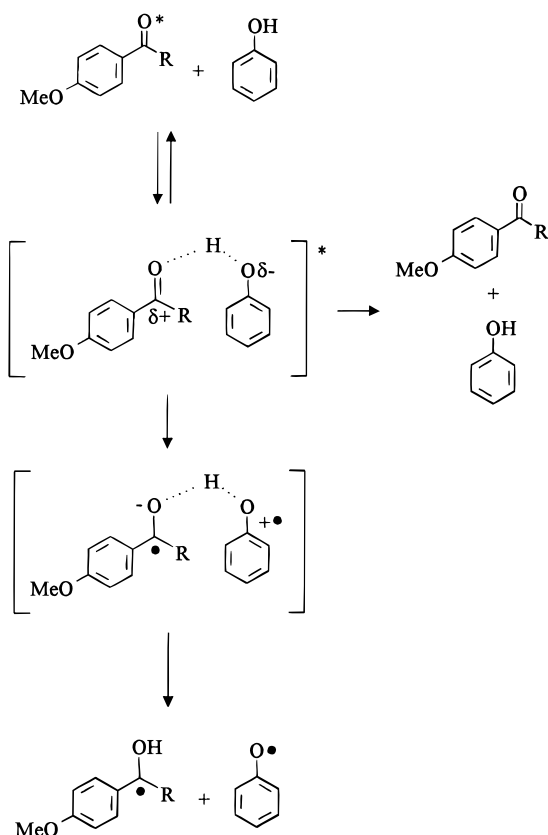
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Scheme 1



that of a *nucleophile*. The most likely way for this to occur is by a mechanism in which hydrogen abstraction is initiated by partial transfer of the phenolic *proton* followed by electron transfer to yield the radical pair, probably via the involvement of a hydrogen-bonded exciplex between the triplet ketone and the phenol. This mechanism is shown in Scheme 1. The facility of such a process would be expected to depend on the acid–base properties of the ketone triplet and the phenol, and the thermodynamics of electron transfer within the hydrogen-bonded complex. As explained below, we suggest that this mechanism is the dominant one for phenolic hydrogen abstraction by lowest  $\pi,\pi^*$  triplet ketones. In the benzophenones, it may require the involvement of the higher energy  $\pi,\pi^*$  triplet state through vibronic mixing; if so, it will become more important as the  $(n,\pi^*)^3 - (\pi,\pi^*)^3$  energy gap is reduced by increasingly strong donor substitution<sup>8</sup> and abstraction by the “normal” mechanism becomes less favorable.

The acid–base properties<sup>30–33</sup> and hydrogen-bonding characteristics<sup>34–37</sup> of aromatic ketone triplets have been studied in detail. Protonation of benzophenone triplets by sulfuric acid in aqueous alcohol<sup>31</sup> or acetonitrile<sup>32,33</sup> solution proceeds rapidly ( $k_{H^+} \sim 5 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ ) and reversibly, and leads to quenching of the triplet via rapid decay of the protonated species by

intersystem crossing ( $k \sim 8 \times 10^7 \text{ s}^{-1}$ ).<sup>33</sup> The  $pK_a$  of the triplet state of benzophenone is +0.18 in aqueous acetonitrile, which should be compared to the ground-state value of  $-5.7$ .<sup>38</sup> This value is considerably higher than would be expected for a ketone with a lowest  $n,\pi^*$  triplet, and it was suggested that protonation involves interactions with the  $\pi,\pi^*$  state.<sup>32,33</sup> This proposal is consistent with earlier evidence, reported by Leermakers and co-workers, that the lowest triplet state of benzophenone has substantial  $\pi,\pi^*$  character in aqueous acids (and other hydroxylic media).<sup>34</sup> Ketones with smaller  $(n,\pi^*)^3 - (\pi,\pi^*)^3$  energy gaps than benzophenone in less polar media (such as acetophenone) or lowest  $\pi,\pi^*$  triplet states (such as xanthone) exhibit significantly higher triplet  $pK_a$  values.<sup>30,32</sup> Electron-donor substituents increase the  $pK_a$  of ground-state benzophenone<sup>38</sup> and would clearly be expected to increase that of the triplet as well (regardless of configuration), in addition to reducing the  $(n,\pi^*)^3 - (\pi,\pi^*)^3$  energy gap.<sup>8</sup>

While phenol is simply not sufficiently acidic to protonate the lowest triplet state of even xanthone to a significant extent, the formation of hydrogen-bonded complexes is likely to be significant, particularly in nonpolar solvents. It certainly is in the ground state, where hydrogen bonding between ketones and phenols in nonpolar solvents is easily detectable by infrared spectroscopy.<sup>18</sup> For example, the reported equilibrium constants for hydrogen bonding of *p*-fluorophenol with benzophenone and *p*-methoxyacetophenone are  $pK_{HB} = 0.97$  and 1.40, respectively, in carbon tetrachloride at 25 °C.<sup>18</sup> The magnitude of the increase in basicity which is expected to accompany excitation of alkoxy-substituted benzophenones and acetophenones to the lowest triplet state suggests that hydrogen bonding to phenol should be orders of magnitude more favorable in the triplet state than in the ground state.

The thermodynamics of electron transfer within a hydrogen-bonded complex can reasonably be expected to lie somewhere between those of two mechanistic extremes: one in which protonation of triplet ketone by phenol precedes electron transfer in the resulting ion pair, and one in which electron transfer precedes transfer of hydrogen as a proton in the resulting radical ion pair. We employ benzophenone for this analysis simply because all of the relevant data are available. The Weller equation<sup>39</sup> predicts that electron transfer from phenoxide ion to protonated benzophenone triplets should be strongly exergonic ( $\Delta G_{et} \sim -44 \text{ kcal/mol}$ ), based on values of +0.24 and  $-0.6 \text{ eV}$  (*vs* SCE) for the standard reduction potentials of phenoxyl radical<sup>40</sup> and protonated benzophenone<sup>41</sup> in acetonitrile, a value of 63 kcal/mol for the triplet energy,<sup>34</sup> and neglecting the Coulombic contribution to  $\Delta G_{et}$ . This contrasts the corresponding free energy for electron transfer from phenol itself ( $E_o \sim +1.65 \text{ V vs SCE}$ )<sup>42</sup> to that of unprotonated benzophenone triplet ( $E_o = -1.83 \text{ V vs SCE}$ ;  $E_T = 69.2 \text{ kcal/mol}$ ;  $\Delta G_{et} \sim +11 \text{ kcal/mol}$ ) in the same solvent. We suggest that the formation of a hydrogen-bonded complex will effectively reduce both the reduction potential of the triplet ketone and the oxidation potential of the phenol to an extent that electron transfer becomes favorable. Following electron transfer, the proton then

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completes its migration to yield the phenoxyl–hemipinacol radical pair. It is relevant to note that phenoxide quenches benzophenones triplets (and those of a number of other aromatic ketones, including 4-methoxyacetophenone) by electron transfer, with rate constants just below the diffusion limit in aqueous acetonitrile solution.<sup>43</sup>

It should be noted that excitation of ground-state hydrogen-bonded complexes cannot contribute significantly to either inter- or intramolecular phenolic hydrogen abstraction in the compounds studied here, given the magnitudes of the reported equilibrium constants for ground-state hydrogen bonding discussed earlier. Indeed, we have found no evidence for ground-state hydrogen bonding in the infrared spectra of **3–6** in CCl<sub>4</sub> solution at low concentrations.

Thus, a mechanism for phenolic hydrogen abstraction which involves electron transfer within a hydrogen-bonded triplet exciplex, followed by proton transfer, is able to explain the unusually high reactivity of  $\pi, \pi^*$  triplet ketones toward phenolic hydrogen abstraction, the negative Hammett  $\rho$  value observed for donor-substituted  $n, \pi^*$  triplet benzophenones, and the deuterium kinetic isotope and solvent effects on the rate of both the intra- and intermolecular<sup>12</sup> processes. The fact that quenching of carbonyl triplets by phenols leads to radical formation with somewhat less than unit efficiency<sup>12</sup> can be explained as due to non-productive collapse of the exciplex to ground-state ketone and phenol by intersystem crossing or by reverse electron transfer within the geminate radical ion pair. The effects of phenol substitution on the rates of intermolecular abstraction by *p*-methoxypropionophenone<sup>12</sup> can also be explained. In general, more highly acidic phenols should lead to more facile hydrogen bonding with the ketone triplet, but the effect on the overall reaction rate is truncated because of an accompanying increase in the oxidation potential of the corresponding phenoxide ion. This would explain why there is no variation in rate with phenol substituent in the quenching of *p*-methoxypropionophenone triplets in benzene solution. We observe a similar lack of sensitivity to phenol substitution in the rate constant for quenching of 4,4'-dimethoxybenzophenone triplets in acetonitrile solution.<sup>44</sup>

The reduction in the rates of bimolecular quenching of **10** and **11** in the presence of water (particularly the latter compound) may be the result of particularly basic lowest triplet states, to an extent that hydrogen bonding to water competes more effectively with that to the phenol. The triplet state behavior of 1-indanone is known to be particularly sensitive to hydrogen-bonding solvents,<sup>37,45</sup> and our experience with **11** suggests that it behaves similarly.

The key feature of this mechanism is the idea that hydrogen bonding between the excited triplet ketone and the phenol has the effect of adjusting the reduction and oxidation potentials of the reactants to the extent where electron transfer becomes thermodynamically favorable. While this is qualitatively the same as invoking a mechanism in which hydrogen abstraction by the carbonyl triplet simply proceeds via a highly polar transition state, it provides a means for  $\pi, \pi^*$  carbonyl triplets to exhibit substantially higher reactivity than they normally do in hydrogen abstraction reactions.

**Geometric Effects on Phenolic Hydrogen Abstraction by  $n, \pi^*$  and  $\pi, \pi^*$  Carbonyl Triplets.** The similar trends in the triplet decay rates of **3**, **4**, and **6** and the rate constants for bimolecular abstraction from *p*-cresol by the corresponding model compounds (**9**, **10**, and **12c**) may indicate that the

optimum geometries for phenolic hydrogen abstraction by donor-substituted  $n, \pi^*$  and  $\pi, \pi^*$  ketone triplets are similar, since the configuration of the lowest triplet state (and its energy) is the only variable in these three compounds. At the very least, it is possible to conclude that the rates of phenolic hydrogen abstraction by donor-substituted  $n, \pi^*$  and  $\pi, \pi^*$  ketone triplets respond identically to the geometric constraints imposed by the common abstracting geometry in the three molecules (see eq 2). This is further borne out by the similarities in the Arrhenius activation parameters for triplet decay of **3** and **6** in acetonitrile. From a structural standpoint, the three compounds are able to form a “sandwich-like” hydrogen-bonded exciplex, involving even perfect in-plane bonding to the carbonyl *n*-orbital, with equal facility.

In the alkoxyindanone derivative (**5**), the carbonyl group is held in an orientation such that in-plane bonding between the phenolic hydrogen and the *n*-orbital is prevented. Interestingly, the rate of intramolecular abstraction in this compound is about half of that in **3**, in spite of the fact that 5-methoxyindanone (**11**) is some 40% more reactive than *p*-methoxyacetophenone (**9**) toward bimolecular abstraction from *p*-cresol. This may suggest that abstraction is fastest when an in-plane arrangement of the phenolic hydrogen and the carbonyl *n*-orbital (in the hydrogen-bonded exciplex) is possible. If intramolecular abstraction in **3** and **5** proceed by identical mechanisms, then one must conclude that the effect is small, but it is similar in magnitude to the analogous geometric dependence of aliphatic hydrogen abstractions by  $n, \pi^*$  triplet ketones.<sup>46–49</sup>

While the triplet lifetime of indanone derivative **5** is significantly longer than that of acetophenone **3**, it is interesting to note that exactly the opposite is true for the corresponding methoxy analogs **7** ( $\tau_T = 0.28 \mu\text{s}$ ) and **1b** ( $\tau_T = 2.6 \mu\text{s}$ ),<sup>13</sup> respectively. In the latter compounds, quenching can only occur by a charge-transfer exciplex mechanism, presumably involving a face-to-face arrangement of the carbonyl (acceptor) and aryloxy (donor)  $\pi$ -systems. The data indicate that this is considerably more efficient in the indanone than in the acetophenone derivative. In **5**, similar interactions (without the prior formation of a hydrogen bond) would be expected to weaken the phenolic O–H bond and facilitate its transfer, presumably with little dependence on geometry at the carbonyl group since it would possess substantial radical anion character. With the difference in triplet lifetimes between **5** and **7** being only a factor of about ten, it is difficult to rule out the possibility that quenching in **5** proceeds by this mechanism. Further support for this derives from the fact that the triplet lifetime of **5** is only slightly reduced in benzene compared to acetonitrile solution, while the solvent effect on the lifetimes of the other three ketones is substantial. If this is true, then the results would imply that the need for in-plane bonding in the hydrogen-bonded exciplex is in fact substantial.

In compounds such as **3–6**, both the ability of the system to form the hydrogen-bonded exciplex and the rate of electron transfer within it would be predicted to also depend on nonbonded electronic interactions between the aromatic  $\pi$ -systems of the triplet ketone and phenol. Future publications will address these aspects of the process, and provide a more detailed examination of substituent and other effects on the rates of

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bimolecular phenolic hydrogen abstraction by  $n,\pi^*$  and  $\pi,\pi^*$  triplet ketones.

## Experimental Section

Acetonitrile (Caledon), methanol (Caledon), and water (Baker HPLC) were all used as received from the suppliers. Benzene (Fisher Thiophene-Free) was purified by extraction with concentrated sulfuric acid, washing to neutrality with water, and distillation from sodium. Ketones **9–12** were obtained from Aldrich Chemical Co. or Lancaster Chemicals and were recrystallized from ethanol/water or ethyl acetate/hexanes. 1,3-Cyclohexadiene and 1-methylnaphthalene (Aldrich Chemical Co.) were distilled. All other compounds were synthesized by modifications of published procedures; details of the syntheses and spectral and analytical data are included in the Supporting Information.

Nanosecond laser flash photolysis experiments employed the pulses from a Lumonics TE-861M excimer laser filled with Xe/HCl/H<sub>2</sub>/He (308 nm, ~12 ns, ca. 40 mJ) or N<sub>2</sub>/He (337 nm, ~6 ns, ca. 4 mJ), or a Lumonics EX-510 excimer laser filled with F<sub>2</sub>/Kr/He (248 nm, ~14 ns, ca. 120 mJ), and a microcomputer-controlled detection system.<sup>16</sup> The system incorporates a brass sample holder whose temperature is controlled to within 0.1 °C by a VWR 1166 constant-temperature circulating bath, or nitrogen gas passed through a dewar filled with liquid nitrogen. Sample temperatures were measured using a Cole-Parmer Type K digital thermocouple thermometer and are accurate to ±0.1 °C.

Samples were contained in cuvettes constructed from 3 × 7 mm (for 248-nm experiments) or 7 × 7 mm Suprasil quartz tubing (Vitro Dynamics), and had an absorbance of ~0.1–0.9 at the laser wavelength. The samples were sealed with rubber septums and deoxygenated with dry nitrogen until constant lifetimes were obtained. Quenchers were added as aliquots of standard solutions.

Steady state photolyses were performed using a Rayonet reactor containing six RPR-300 or RPR-254 lamps and a merry-go-round apparatus (Southern New England Ultraviolet Co.). Nitrogen-purged acetonitrile solutions containing each of **3–6** (0.0025 M) and dodecane

or hexadecane as internal standards were irradiated simultaneously in 10-mm i.d. quartz tubes for periods of time ranging from 10 to 90 min. The samples were analyzed by gas chromatography before, during, and after irradiation under these conditions. No products of retention time shorter than that of the starting materials could be detected in any case. Quantum yields for photolysis of the ketones were estimated by comparing the extent of photolysis of each one to that of **3**.

Phosphorescence emission spectra and lifetimes were measured on a PTI LS-100 luminescence spectrometer, in 4:1 ethanol/methanol glasses at 77 K, using the software supplied by the manufacturer. Spectra were recorded using gated detection and an excitation wavelength of 285 nm. Phosphorescence decay experiments employed an excitation wavelength of 285 nm, and emission wavelengths corresponding to the maximum of the short wavelength 0–0 band of the relevant emission spectrum.

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**Supporting Information Available:** Experimental procedures and characterization data for all new compounds (5 pages). See any current masthead page for ordering and Internet access instructions.

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