

Kinetic and Spectroscopic Study of a Ketyl-Phenoxy Biradical Produced by Remote Hydrogen Abstraction¹

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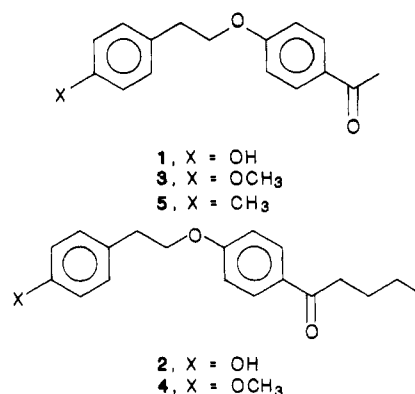
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Laser flash photolysis of **1** in solution leads to the formation of a short-lived triplet ($\tau_T = 13.3$ ns in acetonitrile) which decays via hydrogen abstraction from the remote hydroxy group. The resulting 1,13-biradical has a lifetime of 118 ns in acetonitrile and decays almost exclusively by back-hydrogen-transfer in a process that appears to be controlled by intersystem crossing. The valeryl analogue **2** is nonreactive with respect to Norrish II fragmentation in fluid solution ($\Phi_{II} < 0.001$), presumably as a result of a shortened triplet lifetime due to efficient intramolecular phenolic quenching.

During the last decade biradicals have been the subject of time-resolved studies which have led to a firm understanding of their spectroscopy, reactivity, and the factors that control their lifetimes.³⁻⁵ Studies have concentrated on biradicals of the trimethylenemethane,⁶ Norrish type II (and related),^{4,5} Paterno-Buchi,⁷ and Norrish type I^{8,9} types. With the exception of a few recently reported studies of a series of Norrish type I biradicals derived from 2-phenylcycloalkanones,⁹ virtually nothing is known about transient biradicals with remote radical sites. A possible source of such biradicals is remote hydrogen abstraction by a carbonyl triplet; C-H abstractions of this type are well-known, but reported examples involve long-lived triplets which are not convenient sources for kinetic studies.¹⁰

While 4-alkoxyacetophenones are usually not very good hydrogen abstractors, work from one of our groups has shown that they react very efficiently when the donor is a phenol;¹¹ while the process leads to radical products, it is likely to involve charge-transfer interactions in the transition state. We have now prepared **1** that takes advantage of this property and have examined its photochemistry using laser photolysis techniques. As well, supplementary information on the triplet state behavior of this molecule has been obtained from a study of the Norrish type II reactivity of the valerophenone analogue **2**. In both cases, the behavior of the homologous methoxy derivatives (**3** and **4**) provides an indication of the intrinsic triplet-state properties of the chromophore.



Results and Discussion

Photolysis of a 0.02 M, deaerated acetonitrile solution of **4** results in the expected Norrish II fragmentation products: **3** (quantum yield $\Phi_{II} = 0.13 \pm 0.03$), propene (detected by low temperature GC-MS), and cyclobutanol(s) (detected by VPC analysis and tentatively assigned on the basis of spectral evidence—see Experimental Section). The quantum yield for disappearance of **4** was determined to be $\Phi = 0.24 \pm 0.04$.

Irradiation of a 0.003 M acetonitrile solution of **2**, on the other hand, led to very inefficient photodecomposition, yielding an insoluble tar which was not identified. The quantum yield of disappearance of **2** was $\Phi = 0.009 \pm 0.002$. Since none of the expected Norrish II products were detected, even in solutions taken to ca. 30% conversion, an upper limit of $\Phi_{II} < 0.001$ for the Norrish II fragmentation yield may be estimated.

The Norrish II fragmentation yield for **4** in acetonitrile is comparable to that of 4-methoxyvalerophenone in the same solvent ($\Phi_{II} = 0.14 \pm 0.02$), indicating that the efficiency of the Norrish II reaction of **4** is largely unaffected by the presence of the electron-rich 4-anisyl substituent. Therefore, the nonreactivity of **2** in this solvent may be attributed to efficient intramolecular quenching of the carbonyl triplet state via abstraction of the remote phenolic hydrogen atom, eq 1.

In fluid solvents, the conformational motions which allow these molecules to adopt the sandwich-like quenching conformation are expected to proceed with rates on the order of $2-10 \times 10^8$ s⁻¹,¹² i.e., much faster than the expected¹³ rate of γ -hydrogen abstraction. Slowing down the

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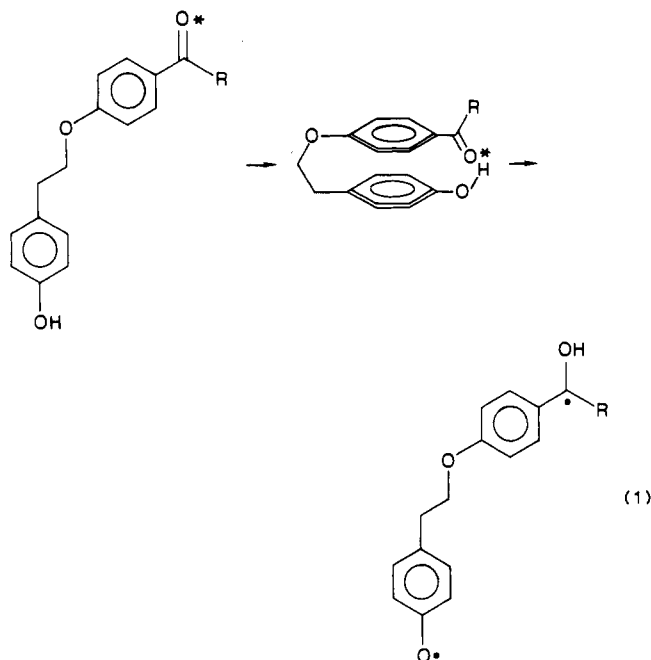
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conformational motions leading to intramolecular triplet quenching in 4 by increasing solvent viscosity or by incorporating the molecule in ordered solvents, such as nematic liquid crystals, leads to an enhancement of Norrish II reactivity by factors of 10 to >150.¹⁴

Under continuous irradiation in deaerated solutions, 1 undergoes photodecomposition very inefficiently, with $\Phi < 0.02$ in benzene or alcohols and only 0.006 in acetonitrile. Again, the product(s) consisted of an insoluble tar which has eluded identification. The methoxy analogue 3 is photoinert under similar conditions.

Laser flash photolysis of 1 in any of these solvents yields intense, short-lived signals in the 400-nm region. In acetonitrile at 293 K, 1 led to the transient spectra shown in Figure 1, which were recorded from 0 to 20 ns and at ~60 ns after the laser pulse. Figure 2 shows a kinetic trace recorded at 400 nm which reveals the presence of more than one transient species. The shorter lived component of the decay can be assigned as the triplet state of 1; it is quenchable by dienes and its spectrum (which predominates in the 0–20 ns time scale) is almost identical with those obtained from 3 and 5 (vide infra) and those reported for other *p*-alkoxyaryl ketones.^{11,15} Kinetic analysis of the two-component decay using a biexponential function led to a 13.3-ns lifetime for the short-lived component and 118 ns for the longer lived species (vide infra). Figure 2 shows the corresponding fit and a plot of residuals.

In experiments using 337-nm excitation, addition of 1-methylnaphthalene (MeN) yields its readily detectable triplet state following triplet energy transfer. In these experiments the triplet of MeN was monitored at 425 nm. The data were plotted in a double reciprocal form, according to eq 2 where A_{425} is the transient optical density at 425 nm, due to the MeN triplet, before significant decay

$$\frac{1}{A_{425}} = \alpha + \frac{\alpha}{k_q \tau_T [\text{MeN}]} \quad (2)$$

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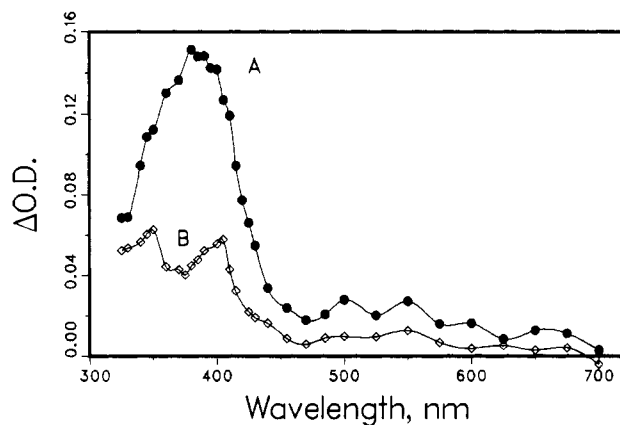


Figure 1. Transient spectra obtained following laser excitation of 1 in acetonitrile. Spectrum A obtained 0–20 ns after the laser pulse. Spectrum B obtained at ~60 ns after the laser pulse.

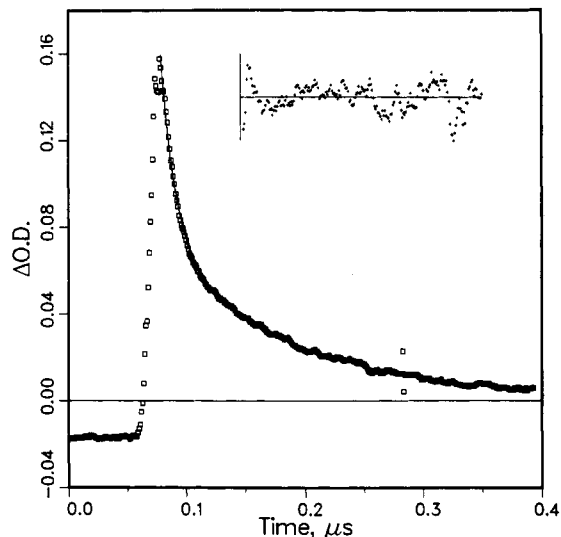


Figure 2. Decay of transient absorption monitored at 400 nm following laser excitation of 1 in acetonitrile. The solid line represents a two-exponential fit of the decay curve (fitting range, points 80 to 285 of 400) leading to lifetime values of 13.3 and 118 ns. The corresponding weighed residuals are shown as an insert.

Table I. Kinetic Parameters and Quenching Data for Triplet 1 and Biradical 6 at 295 K

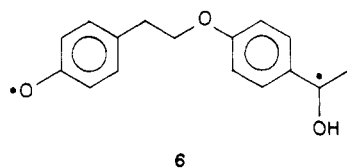
solvent	$k_q \tau_T$ (M^{-1})	τ_T (ns)	τ_B (ns)
acetonitrile	133 ^a 95 ^b	13.3	118
2-propanol	80 ^a	20	85
benzene	37 ^a	<10	100
benzene (H ₂ O sat.)	51 ^a		
benzene (D ₂ O sat.)	92 ^a		
<i>p</i> -dioxane	270 ^a	38	147

^a From 1-methylnaphthalene quenching (see eq 2). ^b Stern–Volmer analysis of biradical yield reduction using 1,3-octadiene as triplet quencher.

takes place, $k_q \tau_T$ is the Stern–Volmer parameter, and α is a constant. We obtained $k_q \tau_T = 133 M^{-1}$ from the intercept-to-slope ratio, which corresponds to a triplet lifetime of ca. 16 ns,¹⁶ in good agreement with the value obtained from the curve-fitting analysis. The kinetic parameters obtained for 1 in acetonitrile as well as in other solvents are summarized in Table I.

(16) Assuming $k_q \sim 8.3 \times 10^9 M^{-1} s^{-1}$. (This value is not unreasonable since it is generally accepted that 1-methylnaphthalene is a more efficient triplet quencher than conjugated dienes.)

The spectrum of the longer lived transient, which decays monoexponentially with $\tau \sim 118$ ns, closely resembles those of typical phenoxyl radicals.¹⁷ The decay kinetics of this transient are not affected by addition of 1,3-octadiene but its yield is considerably reduced; this behavior is that expected for a species which is not an excited triplet but has a triplet precursor. A Stern–Volmer analysis based on this yield reduction leads to $k_q\tau_T = 95$ M⁻¹, in reasonable agreement with the product of the two values.¹⁸ We assign this long-lived transient to the 1,13-biradical (6) generated via intramolecular hydrogen abstraction (see eq 1).



Laser flash photolysis of deaerated, acetonitrile solutions of 3 and 5 led to readily characterized, long-lived triplet absorptions (λ_{\max} 385 nm) with lifetimes of 2.6 μ s and 4.0 μ s, respectively. These triplets were quenched by 1,3-octadiene with $k_q = (6.7 \pm 0.3) \times 10^9$ M⁻¹ s⁻¹.

Thus, the short lifetime of triplet 1 and non-(Norrish II) reactivity of 2 is due to the presence of a mode of decay (eq 1) not available to 3–5. Other *p*-hydroxy ketones are well-known to undergo efficient self-quenching, involving bimolecular, head-to-tail reaction.¹¹ In the case of 1 a study of the concentration dependence (4×10^{-4} to 3.5×10^{-3} M) did not reveal any self-quenching, as could be expected from the low concentrations used and short time scale involved.

While triplet quenchers such as dienes do not affect the biradical lifetime, Tempo (2,2,6,6-tetramethylpiperidine-*N*-oxyl), which along with other nitroxides is known to quench both triplets and biradicals,^{19,20} led to substantial lifetime reductions with $k_q = 3.2 \times 10^9$ M⁻¹ s⁻¹.

Experiments with 1 in 2-propanol resulted in more complex decay kinetics, with apparent triplet lifetimes of 60–80 ns based on a rather poor kinetic fit. Curve-fitting analysis, however, led to lifetimes for two components with $\tau_T = 20$ ns and $\tau_B = 85$ ns; see Table I). Addition of 0.02 M 1,3-octadiene resulted in sufficient triplet quenching to separate the two decays easily, as shown in Figure 3. Under these conditions the triplet lifetime was reduced to 7–8 ns, corresponding to a quenching rate constant for 1,3-octadiene of $\sim 4 \times 10^9$ M⁻¹ s⁻¹. The lifetime of the long-lived component, assigned to the biradical, was unchanged by addition of diene, although these additions did reduce the biradical yield. Stern–Volmer experiments with 1-methylnaphthalene (in the absence of diene) led to $k_q\tau_T = 80$ M⁻¹, corresponding to a triplet lifetime of 20–30 ns, in reasonable agreement with the results of the curve-fitting analysis.

Laser photolysis of 1 in *p*-dioxane gave results which were qualitatively similar to those obtained in 2-propanol. Curve-fitting analysis yielded lifetimes of $\tau_T = 38$ ns and

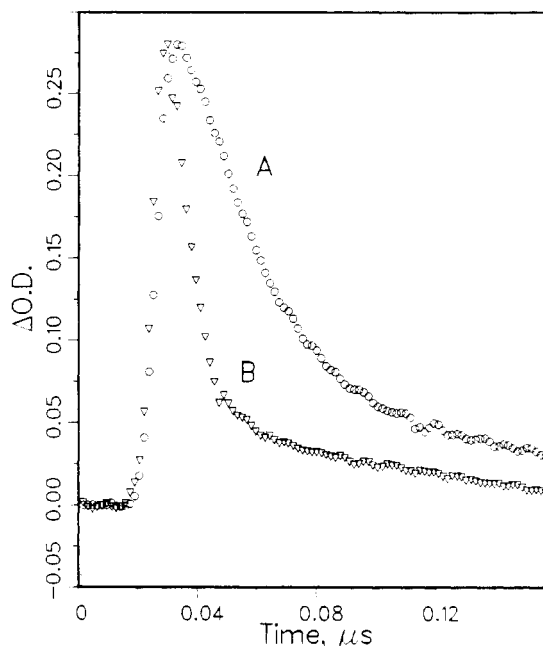


Figure 3. Decay of transient absorption monitored at 390 nm following laser excitation of 1 in 2-propanol. Curve A: in the absence of quencher. Curve B: 0.02 M 1,3-octadiene added.

$\tau_B = 147$ ns (see Table I). Again, addition of 1,3-octadiene sufficiently quenched the triplet to separate the two decays. The addition of diene reduced the triplet lifetime to 20 ns, while the biradical lifetime remained unchanged. Stern–Volmer experiments led to $k_q\tau_T = 270$ M⁻¹ which corresponds to a triplet lifetime of ~ 30 –40 ns, in agreement with the results of the curve-fitting analysis.

Similar experiments in benzene led to a readily identifiable biradical absorption with $\tau_B \sim 100$ ns. Triplet–triplet absorptions were not observable in these experiments. 1-Methylnaphthalene quenching and Stern–Volmer analysis (see eq 2) led to $k_q\tau_T = 37$ M⁻¹ which corresponds to $\tau_T \sim 5$ ns. A residual absorption as large as 40% (at 405 nm) of the biradical absorption was also observed. Despite this, product formation is very inefficient in benzene, suggesting that the transient product responsible for this absorption may regenerate the parent substrate. Clearly, photolysis of 1 in benzene is not as clean a process as in all the other solvents examined. Judging from quantum yields however, any side reaction must be relatively unimportant.

Hayashi et al.²¹ have recently shown that under some experimental conditions xanthone triplets may abstract hydrogen via reaction at the aromatic ring, rather than at the carbonyl oxygen. This type of abstraction leads to cyclohexadienyl rather than ketyl radicals. In order to test for this possibility, the following experiment was performed: a solution of 1 in D₂O-saturated benzene was photolyzed for 30 min using 300-nm lamps. The light dose exceeded by about 10-fold the concentration of reactant, so that each molecule was effectively excited, formed the biradical, and underwent back reaction several times. In spite of this, GC-MS analysis showed no deuterium incorporation in the aromatic ring. We note that back-reaction following ring abstraction from the phenol-*O*-*d* moiety would be expected to lead to considerable yields of deuterium incorporation at the ring positions. We

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(18) From $\tau \sim 14$ ns and $k_q \sim 6.7 \times 10^9$ we obtain $k_q\tau_T \sim 94$ M⁻¹.

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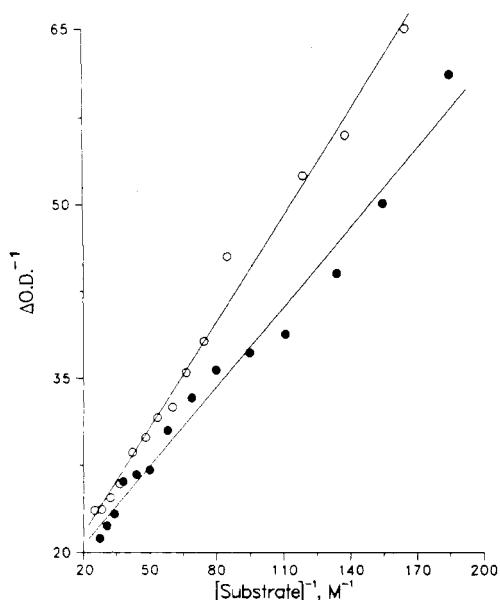


Figure 4. Double reciprocal plot for 1-methylnaphthalene quenching of triplet 1 in H₂O-saturated (○) and D₂O-saturated (●) benzene, according to eq 2.

therefore conclude that biradical formation proceeds via conventional abstraction at the carbonyl oxygen, as indicated in reaction 1.

The triplet lifetimes obtained for 1 are somewhat longer than those that would be expected if conformational motions dominate the rate-determining step(s) for triplet decay.¹² Stern-Volmer studies with 1-methylnaphthalene in benzene and benzene saturated with H₂O and with D₂O led to $k_q\tau_T$ values of 37, 51, and 92 M⁻¹, respectively (see Figure 4), indicating an isotope effect of 1.8 for triplet decay, as well as some effect due to the increased hydrogen-bonding ability of the solvent. These results indicate that phenolic hydrogen abstraction is the rate-controlling step for triplet decay, while the conformational motions involved in achieving the sandwich-like quenching conformation occur on a shorter time scale, as expected from previous studies of intramolecular excimer formation in 1,3-diphenylpropane derivatives.¹²

H₂O and D₂O had no detectable effect on the biradical lifetime, in spite of the fact that its decay also involves hydrogen (deuterium) transfer. This is good evidence that the rate-controlling step for biradical decay is intersystem crossing rather than atom transfer; the efficient quenching by Tempo is also consistent with this hypothesis.²⁰ Caldwell et al.^{8b} have also identified examples where biradical lifetimes are insensitive to deuterium substitution, in spite of the fact that hydrogen (deuterium) transfer was involved in the decay. It was also concluded that intersystem crossing and not hydrogen transfer is the rate-determining step for biradical decay.

Interestingly, application of a 0.2-6 kG magnetic field has no discernible effect on the lifetime of biradical 6. This behavior markedly contrasts that of micellized phenoxyl-ketyl radical-pairs,²² as well as remote alkyl-acyl biradicals⁹ whose lifetimes are subject to substantial magnetic field effects. The behavior of 6 in magnetic fields may indicate that there is substantially more interaction between the radical centers, and hence a much larger singlet-triplet energy gap, than consideration of 6 as a 1,13-biradical would suggest. After all, conjugation imparts some degree of 1,5-biradical character to 6 and the lifetimes

of short biradicals are typically not subject to magnetic field effects.²³

In summary, the photochemical behavior of 1 and 2 provide examples of very fast intramolecular remote hydrogen abstraction, leading to the first direct lifetime measurement for a biradical with an oxygen center and one of the longest through-bond separations between radical sites.²⁴

Experimental Section

Melting points were measured on a Reichert micro-hot stage microscope with polarizing lenses and are corrected. ¹H NMR spectra were recorded in chloroform-*d* solution on a Varian EM390 NMR spectrometer and are reported in parts per million downfield from TMS. Infrared spectra were recorded on a Perkin-Elmer Model 283 infrared spectrometer and are reported in wavenumbers, calibrated against the 1601.8-cm⁻¹ polystyrene absorption. Mass spectra were recorded on a VG Micromass 70-70F mass spectrometer, and exact masses have been calculated by using an atomic mass of 12.00000 for carbon. Ultraviolet absorption spectra were recorded on a Hewlett Packard HP-8451 spectrometer or a Perkin-Elmer Lambda-9 spectrometer equipped with a PE Model 3600 data station. Phosphorescence spectra were recorded on a Perkin-Elmer LS-5 spectrofluorimeter also equipped with a PE-3600 data station and using 7-mm cylindrical quartz sample tubes.

Gas chromatographic separations employed a Varian Model 3700 gas chromatograph equipped with a flame ionization detector, a 2 m × 1/8 in. stainless steel 3% OV-17 (on 80/100 Supelcoport) column, and a Varian CDS-111 integrator. Cyclohexylbenzene was used as the internal standard in all analyses, and the relative detector responses were calibrated. GC-MS spectra were recorded on a Hewlett-Packard 5995 instrument equipped with an OV-101 capillary column. HPLC analyses employed a Gilson isocratic system with a Holochrome variable wavelength detector (at 280 nm). Ethyl acetate (30%) in hexane was used as the eluant (0.5-1.0 mL/min). Preparative liquid chromatography was performed with the same system (50 mL recycling pump head), in conjunction with a 31 × 2.5 cm Merck Lobar Si60 column, ethyl acetate/hexane mixtures, and a 12 mL/min flow rate. For quantitative HPLC analyses, the detector was interfaced to a Unitron microcomputer via an Adalab data acquisition/control card (Interactive Microwave, Inc.), after amplification of the 0-10-mV signal to 0-1 V with an Adaamp analog amplifier. Chromatogram acquisition, storage, and integration was performed by using the Chromatochart software package (Interactive Microwave, Inc.). Dimethyl isophthalate was used as internal standard in all HPLC analyses, after determination of the relative detector responses to it and 1-4.

Nanosecond laser flash photolysis experiments employed the pulses (308 nm; ~4 ns; <80 mJ/pulse) from a Lumonics TE 860-2 excimer laser filled with a Xe-HCl-He mixture and the computerized detection system that has been described in detail elsewhere.²⁴ For 1-methylnaphthalene quenching experiments the pulses (337.1 nm; ~8 ns; <6 mJ/pulse) from a Molecron UV-24 nitrogen laser were used. Samples were contained in 7 × 7 or 3 × 7 mm² cells made of Suprasil quartz (Vitro Dynamics) and were deoxygenated with dry nitrogen prior to the experiments. Sample optical densities were ca. 0.8 at 308 nm, and quenchers were added as aliquots of standard solutions.

Quantum yield determinations were performed with a Rayonet reactor (300-nm lamps) fitted with a merry-go-round, using the Norrish II fragmentation of 4-methoxyvalerophenone (MVP) in benzene as the actinometer with a value of 0.14 for the quantum yield of 4-methoxyacetophenone.^{13a} Solutions were irradiated in 10-mm i.d. quartz tubes, and quantum yields were calculated from the slopes of concentration vs. time plots from runs carried to less than 15% conversion (of MVP). The quantum yields reported

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Table II. Spectral and Analytical Data for Ketones 1-5

ketone	mp (°C)	IR (cm ⁻¹) ^a	¹ H NMR (δ) ^b
1 ^c	106.4-107.4	3619, 2940, 2872, 1682, 1530, 1355, 1240, 1167, 1000, 710, 587	2.51 (s, 3 H), 3.04 (m, 2 H), 4.18 (t, 2 H), 5.47 (s, 1 H), 6.82 (d, 2 H), 6.91 (d, 2 H), 7.15 (d, 2 H), 7.94 (d, 2 H)
2 ^d	95-96	3585, 2920, 1673, 1600, 1572, 1305, 1162, 1000, 970, 552	0.92 (t, 3 H), 1.34 (m, 2 H), 1.68 (m, 2 H), 2.90 (t, 2 H), 3.03 (t, 2 H), 4.17 (t, 2 H), 5.45 (s, 1 H), 6.84 (d, 2 H), 6.92 (d, 2 H), 7.17 (d, 2 H), 7.94 (d, 2 H)
3 ^e	63-64	3005, 2950, 2835, 1682, 1600, 1353, 1239, 1167, 1020, 948, 588, 559	2.53 (s, 3 H), 3.05 (t, 2 H), 3.80 (s, 3 H), 4.20 (t, 2 H), 6.87 (d, 2 H), 6.93 (d, 2 H), 7.23 (d, 2 H), 7.95 (d, 2 H)
4 ^f	49-50	3005, 2953, 2832, 1682, 1600, 1239, 1168, 1020, 618, 560	0.93 (t, 3 H), 1.36 (m, 2 H), 1.70 (m, 2 H), 2.90 (t, 2 H), 3.04 (t, 2 H), 3.80 (s, 3 H), 4.20 (t, 2 H), 6.86 (d, 2 H), 6.93 (d, 2 H), 7.23 (d, 2 H), 7.96 (d, 2 H)
5 ^g	77.8-78.3	<i>h</i>	2.33 (s, 3 H), 2.53 (s, 3 H), 3.07 (t, 2 H), 4.20 (t, 2 H), 6.91 (d, 2 H), 7.18 (s, 4 H), 7.94 (d, 2 H)

^aIR spectra were recorded in KBr (1), chloroform (2), or CCl₄ (3-5). ^bIn chloroform-*d* vs. TMS. ^cCalcd: 256.1099. Found: 256.1085. ^dCalcd: 298.1569. Found: 298.1551. ^eCalcd: 270.1256. Found: 270.1266. ^fCalcd: 312.1725. Found: 312.1724. ^gCalcd: 254.1307. Found: 254.1311. ^hThe spectrum was virtually indistinguishable from that of 3, minus the band at 2835 cm⁻¹.

are the average of two determinations.

Solvents for laser flash photolysis experiments were Aldrich Gold Label in every case and were used as received. Acetonitrile (Caledon HPLC), hexane (Caledon HPLC), ethyl acetate (BDH Reagent), and cyclohexylbenzene (Aldrich) were used as received. Benzene (BDH Reagent) was washed successively with concentrated sulfuric acid, water, and aqueous bicarbonate and distilled from calcium hydride. Acetone (BDH Reagent) was distilled after refluxing over anhydrous potassium carbonate. Pyridine was distilled from anhydrous barium oxide. Dimethyl isophthalate (Aldrich) was recrystallized from methanol (mp 67-68 °C).

Preparation of Compounds. Compounds 1 and 2 were prepared by reaction of 1-bromo-2-[4-(trimethylsilyloxy)phenyl]ethane²⁵ (7) with 4-hydroxyacetophenone and 4-hydroxyvalerophenone, respectively. The preparation and purification of 1 is described in detail below; that of 2 was similar and is not reported. Complete spectral and analytical data for 1-5 are given in Table II.

4-[2-(4-Hydroxyphenyl)ethoxy]acetophenone (1) was prepared by stirring 7 (1.15 g, 4 mmol; from 4-hydroxyphenethyl bromide and chlorotrimethylsilane in dry pyridine²⁵), anhydrous potassium carbonate (0.55g, 4 mmol), and 4-hydroxyacetophenone (Aldrich, 0.54 g, 4 mmol) in anhydrous acetone (10 mL) under reflux for 17 h, after removing the last traces of pyridine from the preparation of 7 by warming under high vacuum (10⁻⁴ Torr) for 6 h. The mixture was cooled, ether (20 mL) was added, and the resulting suspension was washed with 5% aqueous hydrochloric acid (2 × 10 mL) and water (2 × 10 mL), dried over anhydrous sodium sulfate, and filtered. Solvent evaporation yielded a pale yellow oil (1.3 g) which was shown to consist of the desired product and unreacted 4-hydroxyacetophenone by NMR and HPLC. Compound 1 was isolated by cyclic low pressure chromatography, using 10% acetonitrile/dichloromethane as eluant (flow rate of 7 mL/min) and collecting the product after the fourth pass through the column. Evaporation of solvent left a colorless oil which crystallized. Two recrystallizations from chloroform/cyclohexane afforded 1 (0.55 g, 53%) as colorless plates, mp 106.4-107.4 °C. Infrared, ¹H NMR, and mass spectral data for this compound are collected in Table II.

Compounds 3-5 were prepared by reaction of 4'-methoxy-2-phenethyl bromide or 4'-methyl-2-phenethyl bromide with 4-hydroxyacetophenone or 4-hydroxyvalerophenone by a route similar to that of 1 and 2. In each case, the crude product was purified by repeated recrystallization from aqueous ethanol (3 and 4) or hexane (5).

Photolysis of 4 in Deuteriobenzene. A deoxygenated, 0.05 M solution of 4 in deuteriobenzene was sealed in a Pyrex NMR tube and irradiated (300 nm, Rayonet lamps) and the course of the photolysis was followed by NMR. After ca. 85% conversion, the main features of the NMR spectrum were a single methoxy resonance at 3.40 ppm, a singlet at 2.16 (due to 3), a complex doublet at 1.54 (propene), and a doublet at 1.09 ppm in the approximate ratio 4:2:2:1. The propene vinyl protons were also visible as a multiplet centered at 5.00 ppm, as was a broad complex pattern centered at 5.7 ppm. VPC analysis of the photolysate revealed peaks due to 3 and 4 (area ratio = 4.8) and one presumed to correspond to the cyclobutanol(s) (CB) on the basis of its retention time²⁶ and GC/MS results (M⁺ = 312; M - 18). The area ratio of 3:CB was 15.8, indicating that the cyclobutanols undergo some decomposition under our VPC conditions. The cyclobutanols obtained from photolysis of MVP are also unstable under these conditions. The infrared spectrum of the photolysate, after evaporation of the solvent, showed a hydroxylic OH stretch at 3615 cm⁻¹.

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