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Photochemistry and Photophysics of Ketyl Radicals Containing the Anthrone Moiety[1]

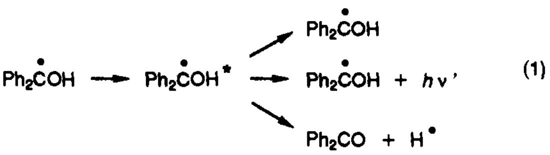
J. C. Netto-Ferreira,[2] W. F. Murphy, R. W. Redmond, and J. C. Scaiano*

Contribution from the Division of Chemistry, National Research Council of Canada, Ottawa, Ontario K1A 0R6, Canada. *Received October 11, 1989*

Abstract: The photochemistry of several ketones containing an anthrone moiety has been employed to produce the corresponding ketyl radicals **1**–**4** by photoreduction in the presence of suitable hydrogen donors. The excited-state behavior of these radicals has been examined with use of two-laser, two-color techniques. The lifetimes for the excited ketyl radicals, ranging from 7.9 ns for **3** to 33 ns for **2**, are longer than that observed for benzophenone ketyl, thus suggesting that conformational restrictions play a key role in controlling excited radical lifetimes. In the case of **3** the dominant mode of decay involves loss of a benzyl radical from the 10-position, while for **1** and **2** the process involves the loss of a hydrogen atom from the hydroxylic position; in the case of **2** this has been confirmed by Raman spectroscopy. The quantum yields of radical photobleaching are 0.20, 0.46, and 0.75 for **1**, **2**, and **3**, respectively, while **4** is essentially photostable. Deuterium substitution at the hydroxylic position leads to a considerable lengthening of the excited-state lifetime. In the case of dibenzylanthrone we have also detected a rather unprecedented (monophotonic) process involving triplet cleavage of a C–C bond at the 10-position, leading to $PhCH_2^•$ and a 10-benzylanthranoxyl radical.

It has been known for at least 15 years that ketyl radicals derived from aromatic ketones, such as benzophenone, are strongly fluorescent.[3-6] During the last few years, the photochemistry of organic reaction intermediates has been the subject of considerable interest and, in particular, ketyl radicals derived from substituted benzophenones have received considerable attention.[7-11]

The ketyl radical from benzophenone, upon photoexcitation, yields its excited state which in nonpolar solvents decays by a competition of radiationless decay, fluorescence, and cleavage of the O–H bond to yield benzophenone and a hydrogen atom (reaction 1).[12]



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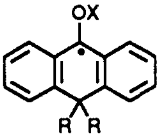
This reaction scheme becomes more complex in polar solvents where the excited ketyl radical has been observed to undergo photoionization.[13] While this and other examples of the photochemistry of reaction intermediates are now well-established, not enough examples have been studied in sufficient detail to establish clear structure–reactivity dependences. In this sense, the subject is sufficiently new that most reports have dealt with either singular examples or limited groups of substrates involving, for example, ring substituents in radicals[14] or carbenes.[15] Our earlier work has suggested that ketyl radicals derived from anthrone[16] may provide a good system in which the effect of basic structural changes can be examined.

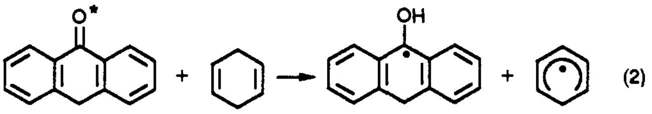
For this report, we have employed two-laser, two-color techniques to examine the photochemistry of radicals **1**–**4**.



1: X = R = H
2: X = H; R = CH_3
3: X = H; R = CH_2Ph
4: X = $SiEt_3$; R = H

Results

Generation of the Radicals. Radicals **1**–**3** were formed by photoreduction of the corresponding ketone. In the case of **1**, photoreduction of **5** in nonpolar solvents yielded the corresponding ketyl radical in a relatively clean reaction. When the solvent employed was not a good hydrogen donor, we employed 1,4-cyclohexadiene as an added hydrogen donor; i.e.:



5* **1** (2)

The photochemistry of **5** can involve complications under conditions where the anthranoxyl radical (**6**) or anthranol (**7**), the enol form of **5**, participate in the reaction. We have reported on these processes in detail elsewhere[17] and, for the present work, have selected conditions where these complications are minimized. The ketone precursors of **2** and **3** (**8** and **9**, respectively) do not present the complications mentioned above, since they do not have hydrogens at the 10-position.

Photoreduction of **8** to yield **2** is straightforward, and in fact, the reactivity of triplet **8** is even higher than that of benzophenone;[18] for example, triplet **8** reacts with 1,4-cyclohexadiene

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(1) Issued as NRCC-30994.

(2) Permanent address: Departamento de Quimica, Universidade Federal Rural do Rio de Janeiro, Rio de Janeiro, Brazil, CEP 23851.

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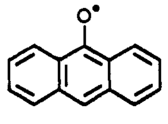

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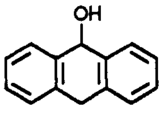

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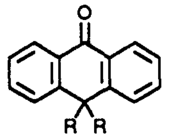
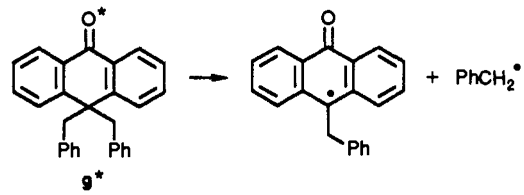


8: R = CH_3
9: R = CH_2Ph

with a rate constant of 6.6×10^8 M^{-1} s^{-1} compared to a value of 2.9×10^8 M^{-1} s^{-1} for benzophenone.[19]

The photochemistry of **9** is slightly more complicated than that of **8**. Thus, in the absence of good hydrogen donors, **9*** undergoes a rare reaction in ketone photochemistry. Wilson et al. have characterized a related example involving a cyclopropane ring opening in a suitably substituted anthrone.[20] The behavior of **9*** is illustrated in reaction 3.



(3)

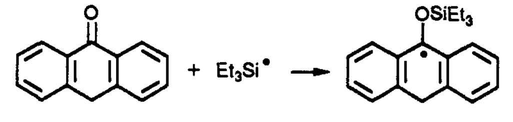
9*

Product studies (vide infra) provide ample evidence for the occurrence of reaction 3. At room temperature in acetonitrile, products are formed with a quantum yield of ~0.01, although this may be a lower limit for the efficiency of reaction 3 since it has not been extrapolated to zero conversion and some of the radicals may back-react to regenerate **9**. Typical triplet lifetimes in the absence of hydrogen donors are around 1 μs.

In the presence of hydrogen donors, **9*** photoreduces readily and, under these conditions, reaction 3 is unimportant. The reactivity of **9*** is very similar to that of **8***; for example, reaction with 1,4-cyclohexadiene occurs with a rate constant of 5×10^8 M^{-1} s^{-1}.

Figure 1 shows the transient absorption spectra for radicals **1** and **3** obtained by photoreduction of the ketone following 308 nm laser excitation. The spectrum for radical **2** has been reported elsewhere[18] and is almost identical with that of **1**. We note that the other radicals produced in the reaction (benzyl or cyclohexadienyl) do not show any significant absorption above 325 nm.

Radical **4** was prepared by a different technique involving the reaction of silyl radicals with the ketone;[21,22] i.e.:



(4)

5 **4**

The radical $Et_3Si^\bullet$ is in turn generated by photolysis of di-*tert*-butyl peroxide in the presence of a high concentration of triethylsilane; thus, the solvent is typically a 1:1 mixture of Bu^tOOBu^t and Et_3SiH. Under these conditions, the *tert*-butoxyl radicals produced photochemically react with triethylsilane (reaction 5) with a rate constant of 5.7×10^6 M^{-1} s^{-1}.[22]

$$Bu^tO^\bullet + Et_3SiH \rightarrow Bu^tOH + Et_3Si^\bullet \qquad (5)$$

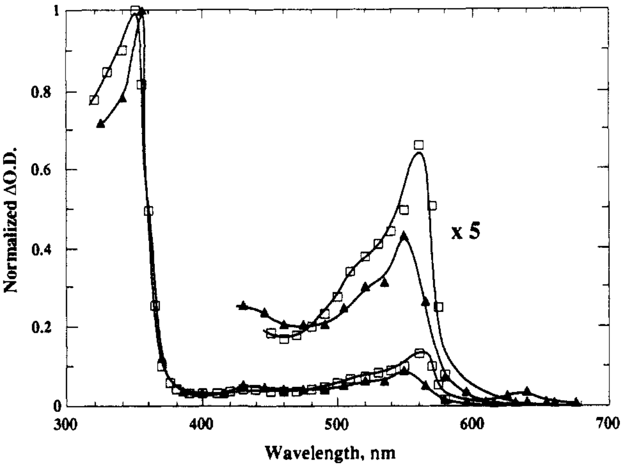


Figure 1. Transient absorption due to **1** (□) and **3** (▲) obtained on 308-nm photolysis of **5** in benzene + 1,4-cyclohexadiene and **9** in toluene, respectively. Spectral resolution is ±2 nm.

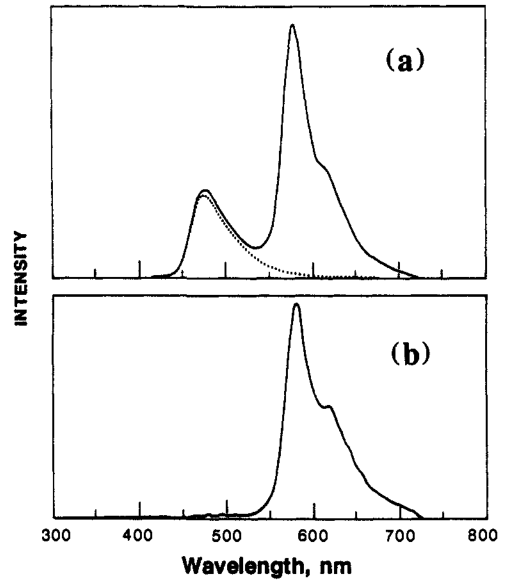


Figure 2. (a) Emission spectrum obtained on 308+337-nm (—) excitation of **5** in benzene + 1,4-cyclohexadiene. Also shown is the spectrum obtained on solely 337-nm (···) excitation. (b) Fluorescence spectrum of excited **1** obtained on subtraction of spectra in (a), also corrected for detector response.

Table I. Fluorescence Properties of Various Anthrone Ketyl Radicals

radical	conditions	λ_{max}, nm	τ, ns
1	benzene, 1,4-cyclohexadiene	580	18
2	toluene	560	33
2-*O-d*	toluene-d_8	560	44[a]
3	toluene	564	7.9
3-*O-d*	toluene-d_8	564	9.7

[a] From ref 16.

Radical Fluorescence Spectra. Radical **1** was excited with the 337-nm pulses from a nitrogen laser following its generation by 308-nm excitation according to the procedures indicated in the previous section. Since some highly fluorescent anthranol is always present, it is important to establish that the spectrum and lifetime recorded are due to **1**, not **7**. The emission spectrum was sufficiently intense that it was necessary to attenuate the signal with a 20% neutral density filter and to employ the smallest slit available in our spectrograph (25 μm).

Figure 2 (top) shows the fluorescence spectra recorded with the 20-ns detection gate coinciding with the 337-nm excitation pulse in two separate experiments. In one, only the 337-nm pulse was employed, in order to produce anthranol (**7**) fluorescence almost exclusively. Under these conditions, the signal peaks at ca. 450 nm and is dominated by the fluorescence mentioned above, along with some minor contribution from phosphorescence from **5**. In the second experiment, the 337-nm pulse was preceded (1.5 μs earlier) by a 308-nm laser pulse which, under these conditions, is absorbed predominantly by the ketone. The delay between laser

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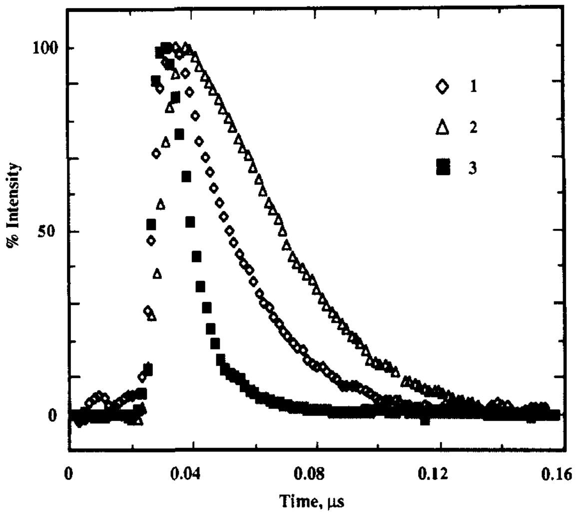

Figure 3. Fluorescence decays at 560 nm on 337-nm photolysis of **1** in benzene and **2** and **3** in toluene following 308-nm photolysis of radical precursors. Lifetimes obtained from the above traces are 18 ns (**1**), 33 ns (**2**) and 8 ns (**3**). Note that for consistency the three traces were obtained with the Molectron (i.e. 8 ns) laser pulse. The lifetime reported for **3** is actually based on an experiment with a PRA nitrogen laser 600-ps pulse.

pulses was chosen so as to allow extensive formation of **1** via reaction 2. The emission is now dominated by a strong band at ~580 nm, while the short-wavelength component remains largely unchanged. Subtraction of the two spectra isolates the contribution from transient species generated by the first (308-nm) laser pulse. This is shown in Figure 2 (bottom) and is attributed to emission from **1**. The spectrum has also been corrected to take into account the wavelength dependence of OMA response.

The emission spectra from **2** and **3** were recorded in the same manner, although in these cases the spectra do not include anthranol emission. The data are summarized in Table I.

Formation of **4** by the technique described above is always accompanied by some photoreduction leading to **1**. The predominant component of this mixture is clearly **4**; however, the emission spectrum and lifetime cannot be easily distinguished from that of **1**. While it is always risky to try to interpret negative results of this type, we believe that this probably reflects a much lower quantum yield for emission for **4** compared with **1**. Naturally, an alternative explanation, which we believe less likely, is that both species have virtually identical spectra and lifetimes.

Radical Fluorescence Lifetimes. These were determined by employing the same two-laser excitation technique (vide supra) but with use of a monochromator/photomultiplier combination for detection. Figure 3 shows typical emission traces recorded for **1**, **2**, and **3**. In the case of **1**, we were also concerned with possible interference from **7**. At 560 nm, where, according to our spectroscopic measurements (vide supra), at least 80% of the emission at this wavelength arises from the ketyl radical, we recorded a lifetime of 18 ns. At 440 nm, where the emission is due to anthranol (**7**), only 337-nm excitation leads to a lifetime of 15.6 ns, i.e., similar to but outside the experimental error of the value given above. To further confirm our value for **1**, we also measured the decay at 620 nm, where **7** cannot interfere, and obtained the same value as that at 500 nm. Lifetime values have also been included in Table I along with the corresponding values for the ketyl-*O-d* radicals in perdeuterated toluene. The expected increase in fluorescence lifetime is observed on going to deuterated solvent, which shows that the O–H(D) bond plays an important role in the deactivation of the excited radicals, even for **3**, which can access the competing deactivation pathway of C–C bond cleavage.

Ketyl Radical Extinction Coefficients. In order to evaluate quantum yields for the photobleaching of the radicals under study (vide infra), it is necessary to know their extinction coefficients at the monitoring wavelength. These are not available in the literature and were determined in this work with Aberchrome-540 as an actinometer for laser experiments in the manner described in earlier work.[23]

Table II. Photobleaching Quantum Yields

radical	solvent	ϵ, M^{-1} cm^{-1} (λ_{bl}, nm)[a]	Φ_{bl}[b]
1	toluene	9150 (360)	0.20
2	toluene	3300 (360)	0.46
3	toluene	6700 (355)	0.75
diphenylketyl	toluene	3300 (550)	0.22[c]
4	1:1 BOOB/Et_3SiH	-	no bleaching

[a] An overall error of 25% is estimated for the extinction coefficients at the wavelength given in parentheses (±2 nm). [b] Estimated error ± 30%. [c] A quantum yield of 0.27 in cyclohexane has been reported earlier.[12]

Evaluation of Photobleaching Quantum Yields. These expermients involved the use of Aberchrome-540 as a two-laser actinometer, employing the techniques reported elsewhere.[12,23] The ketyl radicals were generated by 308-nm laser excitation and were then photolyzed with the pulses from a dye laser tuned to 515 nm. Detection was carried out in the UV band to minimize interference from the strong fluorescence which is unavoidable in the visible region.

In the case of **4**, we have not determined in extinction coefficient, largely because it would have been much more difficult than for **1**–**3**, and given that this radical does not photobleach significantly (vide infra), the measurement is not as important as in the other systems examined.

The results of the measurements mentioned above have been summarized in Table II. It should be noted that the wavelengths listed do not correspond to λ_{max}, but rather to the wavelength where the photobleaching was monitored. In the case of 1,4-cyclohexadiene, it was assumed that the value of 94% hydrogen abstraction efficiency determined for benzophenone[19] also applies to **1**–**3**. Separate experiments in cyclohexane for **1**–**3** (where hydrogen abstraction can be reasonably assumed to be the only quenching mechanism) confirm the ratios of extinction coefficients in Table II. It should be noted that these differences do not reflect differences of a comparable magnitude at λ_{max}, but rather that the monitoring wavelength and λ_{max} have different separations in each case. Figure 1 shows the absorption spectra for the ketyl radicals. All extinction coefficient data have been extrapolated to zero laser dose in the manner described earlier.[12]

We note that photobleaching is also readily observable with 337-nm excitation (the laser wavelength employed for the fluorescence studies of the ketyl radicals), although quantum yields were not determined at this wavelength.

Experiments with **4**, at either 337 or 515 nm, did not show any detectable bleaching at its absorption maximum at 380 nm (where absorption by **1** is negligible). If the detection wavelength is taken further into the UV, where the ketyl radical absorbs strongly, than a significant bleaching can be seen. In these experiments the predominant species is **4**, but there is some contribution by **1**. This is demonstrated by the bleaching observed at detection wavelengths where the anthrone ketyl radical absorbs much more strongly than the adduct radical. In the case of **4**, it is important to note that the absence of observable photobleaching cannot be due to an artifact created by back reaction of $Et_3Si^{\bullet}$ with anthrone ($Et_3Si^{\bullet}$ being a possible photobleaching product), since reaction 4 would simply be too slow to account for significant recovery during the dye laser pulse.[21]

Product Characterization. (a) Raman Spectroscopy. Molecular hydrogen was characterized with use of Raman spectroscopy in a similar manner to that employed in our earlier work.[12] Thus, a deaerated solution of **2** in cyclohexane having an absorbance of 0.3 (0.7 cm optical path) at 308 nm was irradiated by 2000 pairs of 308- and 337-nm laser shots, separated by 2.8 µs. The Raman spectrum of the gas phase above the solution was measured to confirm the presence and amount of hydrogen produced. The

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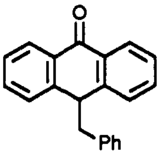
[23] Wintgens, V.; Johnston, L. J.; Scaiano, J. C. *J. Am. Chem. Soc.* **1988**, *110*, 511–517.

strong S_1 (587 cm^{-1}) and S_3 (1034 cm^{-1}) rotational lines and the characteristic vibrational Q branch structure near 4150 cm^{-1} were observed. The area of the S_1 line was measured relative to that of the band at 801 cm^{-1} due to cyclohexane, and, by means of the known scattering cross sections of these two features,[24,25] the hydrogen abundance was determined to be 5.6% that of cyclohexane. From the cyclohexane room temperature vapor pressure and an estimated 2-mL gas volume above the solution, we then find the hydrogen yield to be about 0.5 μmol, where the amount of H_2 remaining in the solution is assumed negligible.[26] In the transient absorption experiment each 308-nm pulse led to a transient optical density of 0.08 at the time of the 337-nm laser pulse, as monitored at 360 nm. This corresponds to a 34 μM concentration of ketyl radicals, of which ca. 28% was bleached by the second laser. Given a typical overlap volume of ca. 30 μL for the two lasers, this corresponds to 0.6 μmol after 2000 shots. The excellent agreement of the H_2 yields from the two types of measurements is perhaps misleading, in that the cumulative error of these calculations is probably 50–60%; in any event, this, combined with the absence of any new products, confirms that the dominant mechanism for bleaching involves elimination of a hydrogen atom.

(b) Product Studies. Lamp irradiation of 0.02 M solutions of **9** in acetonitrile to approximately 10% conversion led to a photolysate containing as major products 10-benzylanthrone (**10**), anthraquinone (**11**), and 1,2-diphenylethane (**12**) in a 1.5:3:1 ratio.

GC analysis of the products of a similar experiment in toluene indicate the formation of two major products, both arising from a photoreductive process: 9,10,10-tribenzyl-9-hydroxy-9,10-dihydroanthracene (**13**) and 9,10-dibenzyl-9-hydroxy-9,10-dihydroanthracene (**14**), as well as a reasonable amount of **12**.



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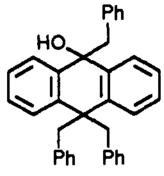

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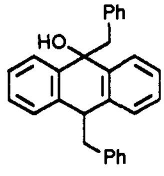

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Discussion

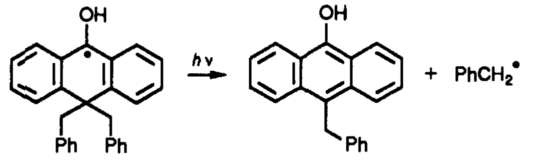
The fluorescence spectra from anthrone-related ketyl radicals (Table I) are rather unexceptional. Substitution by carbon-centered groups at the 10-position leads to a small blue shift and overall the excited-state energy is comparable to that for the benzophenone ketyl.[27] The same applies to the photobleaching quantum yields and the chemical reactions involved in this process; both **2** and the diphenylketyl radical bleach by cleavage of the O–H bond with about the same quantum yield.

A comparison of **1** and **2** indicates that the hydrogen atoms at the 10-position play a role in the radiationless deactivation of **1**. Thus, the quantum yield of photobleaching for **2** is much higher than that from **1**. The same is reflected in the excited-state lifetimes. From the lifetime and quantum yield it is possible to calculate an effective rate constant (k_{eff}) for the photocleavage, i.e.

$$k_{eff} = \Phi_{bl}/\tau \tag{6}$$

The values of **1** and **2** are 1.1 and 1.4 × 10^7 s^{-1}, respectively. The fact that these values are essentially the same supports the idea that the substituents at the 10-position affect the internal conversion of the excited radical, but not the chemical decay of **1** and **2**.

The situation above contrasts with the case of **3**, where the two benzyl moieties at the 10-position determine the overall excited-state behavior. Here the value of k_{eff} is 9.5 × 10^7 s^{-1}. The large increase in k_{eff} is accompanied by a change in mechanism, leading to cleavage of the C–C bond at the 10-position (reaction 7).



9 **15** (7)

Note that **15** is simply the enol form of **10**: in nonpolar solvents we expect reketonization to lead predominantly to **10**. Judging from the rate constants given above, one would anticipate some O–H cleavage (leading to the parent ketone) to compete with reaction 7. If this is the case, it would be hard to detect, since it would probably be a minor pathway which does not yield a new product.

Interestingly, **4** is essentially photostable. While it is not possible to carry out an analysis similar to that given above for **1–3**, since we could not determine a lifetime, is seems reasonable to assume that k_{eff} should be smaller than 10^7 s^{-1}. While failure of the strong Si–O bond to cleave is not unexpected, failure to observe cleavage of the C–H bonds at the 10-position to yield a substituted anthracene is rather surprising, since this process is probably exothermic from the excited-state surface.

The Raman experiments described above leave no doubt that the decay mode for **2** involves O–H cleavage, just as in the case of benzophenone ketyl radical.[12] For the diphenylketyl, the value of k_{eff} in nonpolar solvents can be estimated as ca. 6 × 10^7 s^{-1}. Thus, the fact that the quantum yield is higher in the case of **2** (see Table II) tends to obscure the fact that from a kinetic point of view cleavage is favored in the case of the diphenyl ketyl. The reasons for this preference are not clear.

The chemical decay paths for **1–4** show quite clearly that two-photon processes can be highly selective processes. This contrasts with the frequent (and unjustified) perception that two-laser excitation of organic samples can lead to indiscriminate fragmentation. While substitution at nonreactive centers (compare **1** and **2**) does not change the value of k_{eff} significantly, it can have a significant effect on products yields.

Finally, the photochemistry of **9** in non-hydrogen-donating solvents provides a rare example of remote C–C bond cleavage in carbonyl compound photochemistry. Clearly, the process is driven by the aromatization of the ring system. While the quantum yield of reaction 3 is rather low, its chemical yield is quite high.

Experimental Section

Materials. The solvents benzene (Aldrich), acetonitrile (Fisher), and toluene (Fisher) were used as received, and di-*tert*-butyl peroxide (MCB) was passed through an activated alumina column immediately prior to use. 1,4-Cyclohexadiene (Aldrich) was distilled prior to use and triethylsilane (Aldrich) was used as received.

10,10-Dibenzylanthrone and 10,10-dimethylanthrone were synthesized by a literature procedure,[28] chromatographed on silica gel, and recrystallized from acetone/water and hexane, respectively. Both compounds have melting points in agreement with literature values and their spectroscopic characteristics agree with the proposed structures. Anthrone (Aldrich) was used as received. Aberchrome-540 was purchased from Aberchromics Ltd. (Cardiff) and used as received.

General Techniques. Ultraviolet absorption spectra were recorded with a Hewlett-Packard 8451-A diode array spectrophotometer. GC analyses were done on a Perkin-Elmer 8320 capillary gas chromatograph with a 12-m silica BP1 column. GC/MS analysis were performed on a Hewlett-Packard 5995 instrument equipped with a 10-m Ultra-1 (OV-101) capilllary column. Melting points were determined in a Mel-Temp apparatus and are not corrected.

Raman Spectroscopy. Raman spectra were excited by about 3-W of 514.5-nm radiation from a Coherent Radiation CR-12 argon ion laser. The sealed irradiation cell was inverted and mounted so the focussed laser beam intersected the fused-silica cell walls above the liquid surface at about the Brewster angle. The intensity of the observed spectrum was

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enhanced by double-passing the incident beam pack through the cell and by collecting the back-scattered light, both with appropriate spherical mirrors. Spectra were observed with a Spex 14018 double monochromator with a cooled RCA C31034 photomultiplier and recorded with a Spex Datamate system. The spectral slit width was 2 cm^{-1}, and 10 scans (1-s data period, 0.5 cm^{-1} step size) were taken, alternating between the hydrogen and cyclohexane bands, for improved sampling statistics. The two bands observed are so close in frequency that no correction was made for the variation in detection sensitivity; this introduces an error of at most 1 or 2 % in the value of the relative abundance.

Product Studies and Quantum Yield Determinations. Deaerated samples of **9** in acetonitrile or toluene were irradiated through Pyrex with Rayonet RPR-3000 300-nm lamps. Products were identified by comparison of GC/MS spectra with those of authentic samples except for the cases of **13** and **14** where standards were not available. The following mass spectra data are consistent with the proposed structures: 10,10-Dibenzylanthrone (**9**) *m/z* (%) 374 (22.7, M$^+$), 283 (100, M$^+$ - 91), 91 (7.6); 10-benzylanthrone (**10**) 284 (30.9, M$^+$), 193 (100, M$^+$ - 91), 165 (25.7), 91 (22.8); **13** 466 (<1, M$^+$), 448 (4.9, M$^+$ - 18), 357 (100), 266 (9.7), 279 (17.5), 265 (21.2); **14** 376 (<1, M$^+$), 359 (30, M$^+$ - 17), 358 (100, M$^+$ - 18), 267 (25.2).

Quantum yield determinations were conducted with use of the formation of acetophenone from valerophenone as an actinometer and by taking the quantum yield for formation of acetophenone as 0.3 in benzene at room temperature.[29] The samples were contained in Pyrex tubes and deaerated by bubbling with oxygen-free nitrogen.

Laser Flash Photolysis Studies. Experiments were performed with use of either static cells or a flow system. In the case of 10,10-dibenzylanthrone it was necessary to use a flow cell due to absorption by the products formed. The flow was controlled such that each pulse irradiated a fresh volume of solution.

A Lumonics TE-860-2 excimer laser (308 nm, ~5 ns, ≤40 mJ/pulse) was used in both one- and two-laser experiments as the synthesis laser for the ketyl radical under study. For the measurement of fluorescence spectra and decays, the ketyl radicals formed on 308-nm laser excitation were then excited by pulses from either a Molectron UV-24 (337.1 nm, ~8 ns, ≤10 mJ/pulse) or a PRA-LN-1000 (337.1 nm, ~600 ps, ≤1 mJ/pulse) nitrogen laser. Fluorescence spectra were recorded with a gated-intensified Series 3 optical multichannel analyzer (OMA) from E.G.&G. and normally employed excitation by the Molectron laser. Fluorescence decays were monitored with the same equipment (vide infra) employed for transient absorption kinetics and required the use of the PRA nitrogen laser for the shorter lifetimes. Transient absorption spectra were recorded with OMA detection as indicated above, or by the "point-by-point" approach that is common in laser photolysis work. The system employed for the latter measurements, as well as for all kinetic studies, utilizes an R-7912 Tektronix transient digitizer to capture the data from a monochromator/photomultiplier (RCA-4840) system. The data is then transferred to a PDP 11/23$^+$ computer that also controls the experiment and provides adequate processing facilities. Further details have been reported elsewhere.[30,31]

The determination of extinction coefficients for the anthrone ketyl radicals was carried out with reference to the actinometer system of Aberchrome-540. The wavelengths are accurate to ±2 nm while the bandwidth is 1 nm. On 308-nm photolysis, the colored form is produced with a quantum yield ($\Phi_{\mathrm{I-II}}$) of 0.20 in toluene and has an extinction coefficient (ϵ_{II}) of 8200 M^{-1} cm^{-1} at its $\lambda_{\max}$ of 494 nm. The quantum yield of formation of the anthrone ketyl radicals (Φ_{AnK}) under our conditions is assumed to be 0.94.[19] The extinction coefficients of the anthrone ketyl radicals (ϵ_{AnK}) are given by the expression:

$$\epsilon_{\mathrm{AnK}} = \frac{\Delta\mathrm{OD(AnK)}}{\Delta\mathrm{OD(II)}}\frac{\Phi_{\mathrm{I-II}}}{\Phi_{\mathrm{AnK}}}\epsilon_{\mathrm{II}} \qquad (8)$$

where ΔOD(AnK) and ΔOD(II) are transient absorbances following 308-nm photolysis of optically matched samples of ketone and Aberchrome-540 in toluene at the laser wavelength of 308 nm, respectively. Improved accuracy was achieved by measuring transient absorbances as a function of laser dose. The ratio of the measured slopes at the origin (i.e. as the laser dose approaches zero) was substituted for the first term on the right hand side of the equation, along with other known values, to allow the determination of the extinction coefficient of the anthrone ketyl radicals at the given detection wavelengths. Note that while this approach ensures that the extinction coefficients were determined under conditions of exclusively monophotonic excitation *and* linear detector response, the spectra of Figure 1 are recorded at high laser dose and may include minor spectral distortion, affecting particulary the UV to visible ratio of intensities.

The quantum yields of photobleaching of the anthrone ketyl radicals in toluene were measured with use of Aberchrome-540 in toluene as the two-laser actinometer. The experiment was done in the following manner:

(i) Kinetic traces arising from 308-nm excitation of solutions of both anthrone and Aberchrome-540 in toluene were recorded at the dye laser emission maximum of 515 nm. This was repeated for different 308-nm laser energies, controlled with use of a series of calibrated neutral density filters. This permits the measurement of transient absorbance at the dye laser wavelength at the exact time of the dye laser pulse ($\Delta\mathrm{OD}_t$).

(ii) Kinetic traces arising from 308 nm followed by 515-nm excitation of the above systems were recorded at the wavelengths given in Table II and at 494 nm for the anthrone ketyl radicals and the colored form of Aberchrome-540, respectively. Again this was done for each 308-nm laser dose. The dye laser energy was constant in each case. From these traces the bleached transient absorbances ($\Delta\mathrm{OD}_{\mathrm{bl}}$) were determined, where

$$\Delta\mathrm{OD}_{\mathrm{bl}} = \Delta\mathrm{OD}_1 - \Delta\mathrm{OD}_2$$

and $\Delta\mathrm{OD}_1$ and $\Delta\mathrm{OD}_2$ are transient absorbances immediately before and after the dye laser pulse.

(iii) The quantum yield of photobleaching (Φ_{bl}) of the anthrone ketyl radicals, under conditions of optical matching of radical and Aberchrome-540 at the time of the dye laser pulse, is given by

$$\Phi_{\mathrm{bl}}(\mathrm{AnK}) = \frac{\Delta\mathrm{OD}_{\mathrm{bl}}(\mathrm{AnK})}{\Delta\mathrm{OD}_{\mathrm{bl}}(\mathrm{II})}\frac{\epsilon_{\mathrm{II}}}{\epsilon_{\mathrm{AnK}}}\Phi_{\mathrm{bl}}(\mathrm{II}) \qquad (9)$$

where ϵ_{AnK} and ϵ_{II} are extinction coefficients of both species at the respective detection wavelengths (ϵ_{II} is 8200 M^{-1} cm^{-1} at 494 nm); Φ_{bl}(II) is the quantum yield of photobleaching of the colored form of Aberchrome-540, which has the value of 0.054 at the excitation wavelength of 515 nm.

It is somewhat more accurate to replace the first term on the right side of the equation with the ratio of the slopes obtained from plots of $\Delta\mathrm{OD}_{\mathrm{bl}}$ vs $\Delta\mathrm{OD}_t$ for both sample and reference. This ratio should be statistically more accurate than that obtained from a single matched absorbance. This procedure was used to evaluate the quantum yield of photobleaching of the anthrone ketyl radicals in toluene.

Photobleaching studies were carried out with use of a Candela flash pumped dye laser operated at either 420 nm (Stilbene 420 dye) or 515 nm (Coumarin 503 dye) as the second laser. The relatively long pulse (~250 ns, ≤250 mJ/pulse) tends to minimize the occurrence of two-photon processes induced by the dye laser alone. Two-laser product studies used a combination of 308- and 337-nm excitation from the excimer and nitrogen lasers described above.

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