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Photoenolization of *o*-Alkyl-Substituted Carbonyl Compounds. Use of Electron Transfer Processes to Characterize Transient Intermediates

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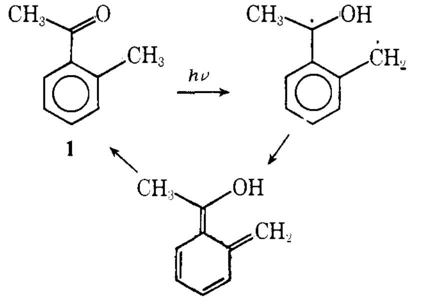
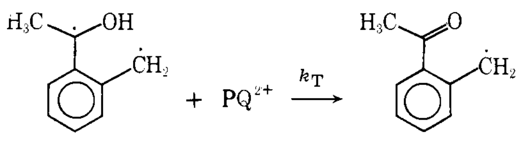
Abstract: Intramolecular hydrogen transfer in photoexcited *o*-methyl-substituted carbonyl compounds leads to the formation of short-lived biradicals which decay to yield unstable enols. The biradicals can be trapped with suitable electron acceptors, and a study of these processes leads to the measurement of biradical lifetimes, quantum yields, and their rates of electron transfer. The combination of these studies with quenching of the process by 1,3-pentadiene leads to the evaluation of the number and lifetime of the triplet state precursors. Ground-state conformation plays an important role in determining the nature and kinetics of triplet state processes. In a typical example, *o*-methylbenzaldehyde, two triplet states are responsible for biradical production; they have lifetimes of 1.1 and 95 ns in wet acetonitrile and account for 58% and 42% of the reaction, respectively. The biradicals are generated with a quantum yield of 0.83, live 1500 ns, and transfer an electron to paraquat dications with a rate constant of 6.2×10^9 M^{-1} s^{-1}.

The photochemistry of *o*-methylacetophenone and several other *o*-alkyl-substituted carbonyl compounds has been the subject of several studies by steady-state irradiation, as well as flash techniques.[2-15] In general, these studies have led to consistent and reproducible results; nonetheless, the interpretation of those results has been the subject of considerable controversy, reflecting largely the assignment of the same transient signals to different species. Reaction 1 shows a simplified mechanism in the case of *o*-methylacetophenone, **1**.



(1)

When the syn-anti rotational equilibrium in the ground state is taken into consideration, the number of species potentially involved in the reaction includes: two ground states, two singlets, two triplets, two enols, and at least one biradical;[3] further, the biradical can be either described as such or as the triplet state of the enol. During the last few years, several groups have proposed techniques which allow the characterization of some of the species involved in the reaction. For example, Wagner[3] has used the triplet sensitized isomerization of dienes to measure triplet lifetimes and quantum yields of intersystem crossing. Wirz[4] has proposed the use of hexamethylphosphoric acid triamide (HMPA) to characterize the *Z* enols, since this solvent produces a considerable retardation of the reketonization. In a preliminary communication from this laboratory,[11] we proposed the use of electron transfer properties of the biradical in order to measure its lifetime, as well as establish the nature and number of its precursors. For example, reaction 2 shows the reaction with paraquat (1,1′-dimethyl-4,4′-bipyridilium, PQ^{2+}) dications.



$+ PQ^{+}\cdot + H^{+}$ (2)

The intense blue color of the radical ion $PQ^{+}\cdot$ makes it very easy to characterize (λ_{max} 603 nm);[16] if its formation is monitored in time-resolved experiments, the corresponding time profile contains information on the biradical lifetime, τ_B, as well as the rate constant for electron transfer, k_T.

In this paper, we report a study of the photochemistry of **1-6** in wet acetonitrile using the technique described above. We have been able to measure the biradical lifetimes, the quantum yields with which they are produced, Φ_B, their electron donor ability (k_T), the triplet lifetimes, and, when applicable, the syn:anti conformation ratio in the triplet state. Our approach, while indirect, overcomes the problem of transient assignment since, provided the triplet lifetime(s) are short, the only good

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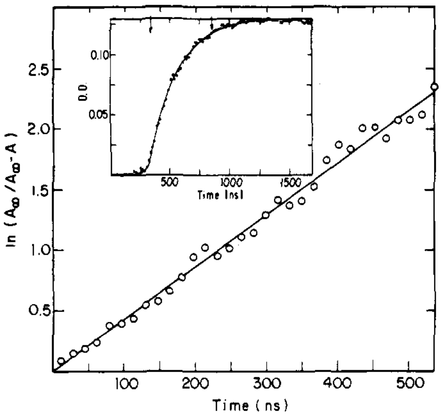


Figure 1. Plot according to eq 4 for **1** (0.06 M) and PQ^{2+} (4.73×10^{-4} M) in wet acetonitrile. (Insert) Time profile for the buildup of transient absorbance (at 603 nm) due to $PQ^{+}\cdot$. The two arrows indicate the region used for the least-squares treatment shown in the main part of the figure.

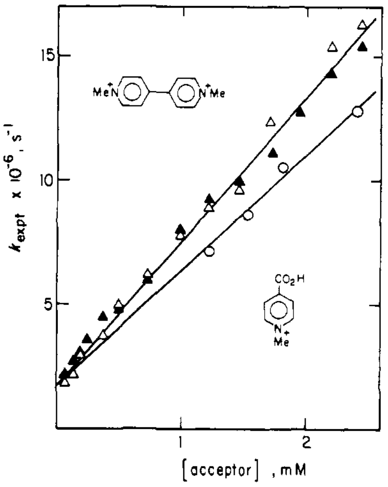
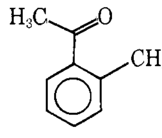
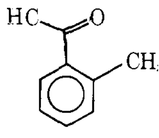


Figure 2. Kinetic data for the trapping of the biradical from **1** by PQ^{2+} (△) and by **7** (○). The full triangles correspond to PQ^{2+} in the presence of 0.1 M *trans*-1,3-pentadiene.

electron donor is the biradical. Only in the case of **5** is the triplet lifetime long enough to interfere with the measurements.



1



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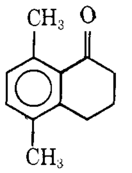

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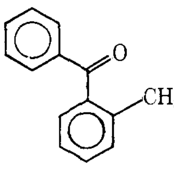

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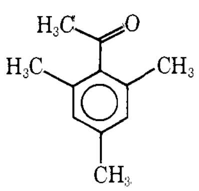

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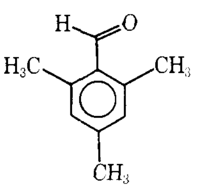

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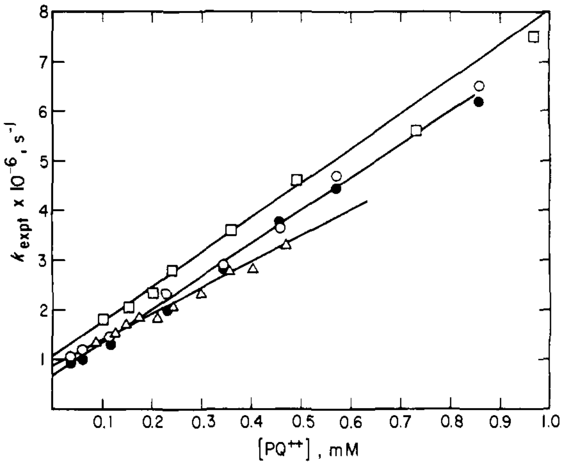


Figure 3. Trapping of the biradicals from **2** (○ and ●), **3** (□), and **6** (△) by PQ^{2+}. The full circles correspond to **2** in the presence of 0.1 M *trans*-1,3-pentadiene.

Results

Deaerated samples of **1-6** in a 1:4 water:acetonitrile (v/v) mixture were irradiated with the pulses (337.1 nm, 8 ns, 3 mJ) from a nitrogen laser. Transient absorptions were monitored by using a detection system with nanosecond response (see Experimental Section). Most of our results were obtained from studies of the electron-transfer reaction between the biradical and paraquat dications, e.g., reaction 2. The details of this technique have been discussed elsewhere.[17,18]

The applicability of the technique depends both on the reactivity of the biradicals, as well as on the unreactive character of the ground-state enols. We could not find any evidence for reaction between enols and PQ^{2+}, at least in the time scale examined in our experiments. The formation of enols is evident in many systems, and, in particular, we examined their behavior toward PQ^{2+} in the case of **4**, where the short biradical lifetime (vide infra) and the convenient position of the absorption bands make the experiment quite simple. Examination at 603 nm did not reveal the formation of any radical ions other than those generated in the first 100 ns, which are attributed to the biradical. The photoenols, in particular, the long-lived anti conformer, were also found in the presence of PQ^{2+} (monitored at 435 nm), and the kinetics of their decay were insensitive to the addition of PQ^{2+}. The ground-state photoenols will therefore be assumed to be unreactive toward the electron acceptors used. The formation of $PQ^{+}\cdot$ can be monitored at one of the absorption maxima,[16] typically 603 nm. The insert in Figure 1 shows a typical buildup profile following laser excitation. The formation of $PQ^{+}\cdot$ follows pseudo-first-order kinetics; fitting of the corresponding time profile leads to k_{expt}, the experimental pseudo-first-order rate constant associated with the buildup of the radical ions. As pointed out above, k_{expt} is related to the rate of trapping k_T and the biradical lifetime, τ_B, eq 3.[17]

$$k_{expt} = \tau_B^{-1} + k_T[PQ^{2+}] \qquad (3)$$

For the method to be useful, an important condition must be met: the triplet lifetime τ_T must be substantially shorter than τ_B. This criterion is met by the systems under study (vide infra), with the possible exception of **5**. Figure 1 illustrates the evaluation of k_{expt} from the experimental transient absorbance according to eq 4

$$\ln \frac{A_\infty}{A_\infty - A} = k_{expt}t \qquad (4)$$

where A_∞ and A are the optical densities in the "plateau" region (see insert in Figure 1) and at time t, respectively. Figures

Table I. Summary of Kinetic Parameters[a]

substrate	τ_B[b]	Φ_B[c] (Φ_{isc})[d]	$\tau_T(1)$[e]	$\tau_T(2)$[e]	$10^{-9}k_T$[f]	syn:anti
1	580	0.60 (0.7)	0.5	34	6.5	73:27
2	1500	0.83 (0.86)	1.1	95	6.2	58:42
3	930	0.80	4.5	*g*	5.6	*g*
4	24	*h*	0.2[i]	*h*	*h*	*h*
5			(300)			
6	1100	0.84 (0.96)	1.6	*g*	5.2	*g*

[a] In 1:4 water:acetonitrile (v/v) at room temperature, unless otherwise indicated. [b] In nanoseconds; typical errors are 10–20%. [c] Using γ-methylvalerophenone as a standard (see text); errors ca. ±10%. [d] The quantum yields of intersystem crossing were determined from the transient yields of triplet 1-methylnaphthalene produced when it was added as a quencher. The values were obtained from the intercepts of plots of (signal due to 1-methylnaphthalene triplet)$^{-1}$ vs. [1-methylnaphthalene]$^{-1}$. Acetophenone was used as a reference substrate with $\Phi_{isc} = 1$. [e] In nanoseconds; typical errors ca. 15%. [f] In units of M^{-1} s^{-1}. [g] Only one triplet state. [h] Not measured; see text. [i] In benzene; from ref 3.

2 and 3 show the evaluation of τ_B and k_1 according to eq 3. In the case of the biradical from **1**, we have also used 4-carboxy-1-methylpyridynium (**7**) as an electron acceptor. The corresponding data leading also to τ_B and k_T has been included in Figure 2. The intercept is independent of the nature of the electron acceptor, as expected. The values of k_T are 6.5 × 10^9 M^{-1} s^{-1} for PQ^{2+} and 4.9 × 10^9 M^{-1} s^{-1} for **7**.

The values of τ_B and k_T have been summarized in Table I. In the case of **5** we only observe weak signals from PQ$^{+\cdot}$, but it seems probable that these arise via electron transfer involving the triplet state rather than a biradical process (see below).

If 1,3-pentadiene is added to a sample containing a photoenolizable carbonyl compound and PQ^{2+}, the experimental kinetics, as measured by k_{expt}, do not change (see Figures 1–3) but the values of A_∞ decrease, reflecting the quenching of the precursor triplet state (or states).[18,19] In the case of **3** and **6**, the quenching of the "plateau" absorbance follows a simple Stern–Volmer dependence, Figure 4, and eq 5.

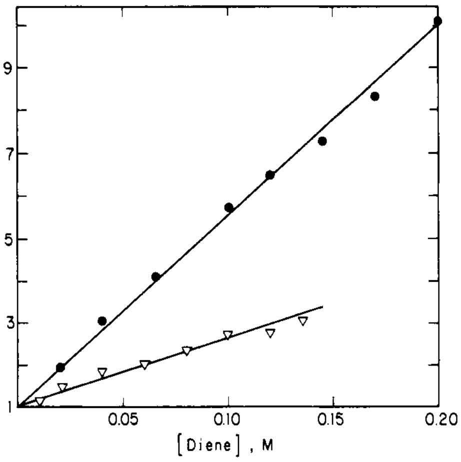
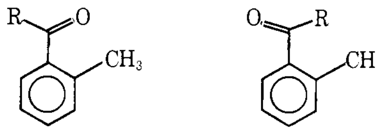


Figure 4. Stern–Volmer plot according to eq 5 for **3** (●) and **6** (▽). The quencher is *trans*-1,3-pentadiene.

$$\frac{A_\infty^0}{A_\infty} = 1 + k_q\tau_T[Q] \qquad (5)$$

[Q] is the triplet quencher concentration and k_q the rate of triplet quenching (1 × 10^{10} M^{-1} s^{-1} in the solvent used).[18] The values of τ_T derived from these plots are also shown in Table I.

In the case of **1** and **2**, the addition of diene does not lead to simple Stern–Volmer behavior, and the corresponding plots (Figure 5) are nonlinear. The presence of regions with two distinct slopes reflects the involvement of two excited states in the reaction. These can be assigned to the syn and anti conformers of the corresponding triplet states.[3]



syn (*Z*) anti (*E*)

1, R = CH$_3$
2, R = H

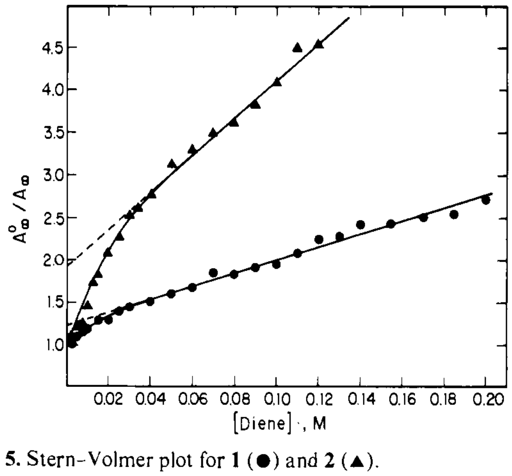


Figure 5. Stern–Volmer plot for **1** (●) and **2** (▲).

Wagner[3] has proposed that the short-lived triplet should be assigned to the syn conformer, while the longer one is the anti conformer which must undergo bond rotation prior to hydrogen transfer.

The same type of triplet state isomerism could be expected in the case of **4**. The short biradical lifetime (τ_B = 24 ns, corresponding to the *A* transient in Porter's nomenclature[6]) makes it virtually impossible to reach any conclusion regarding the nature and number of triplet states. In fact τ_B is small enough to make the last term in eq 3 negligible in comparison with τ_B^{-1} and as a result we were unable to obtain a reliable value of k_T for the biradical from **4**. The quantum yield of trapping and hence the signal intensity are quite small reflecting the short biradical lifetime, a low yield of biradical formation, Φ_B, or both.

$$\text{yield of trapping} = \Phi_T = \Phi_B \frac{k_T[\mathrm{PQ}^{2+}]}{\tau_B^{-1} + k_T[\mathrm{PQ}^{2+}]} \qquad (6)$$

The relative importance of the syn and anti conformation in triplets **1** and **2** can be derived from an analysis of the plots in Figure 5, and these conformations have also been included in Table I. The lifetimes of the syn and anti triplets [$\tau_T(1)$ and $\tau_T(2)$, respectively] were determined from the plot of (A_∞^0/A_∞) vs. diene concentration, Figure 5. The plateau absorbance, A_∞, due to PQ$^{+\cdot}$ is proportional to the contribution from both rotational conformations according to eq 7.

$$A_\infty = (I_0\epsilon l)f_{BT} \times \sum_{i=1,2} f_s(i)\Phi_{isc}(i)(1 + k_q\tau_T(i)[\text{diene}])^{-1} \quad (7)$$

The first term, $I_0\epsilon l$, is the product of the light intensity absorbed (in einstein L^{-1} s^{-1}) times the extinction coefficient for $PQ^{+}\cdot$, times the optical path; f_{BT} is the fraction of biradicals trapped, as given by the last term in eq 6; $f_s(i)$ are the relative fractions of syn and anti singlets and should reflect the ground-state conformation, and $\Phi_{isc}(i)$ are the quantum yields of intersystem crossing for both singlet conformers. At relatively high diene concentrations the long-lived triplet is virtually completely quenched and the ratio of slope to intercept of the linear portion (see Figure 5) gives $k_q\tau_T(1)$. The lifetime of the long-lived triplet was derived by subtracting the extrapolated $A_\infty/A_\infty{}^0$ values from the experimental ones and plotting the reciprocal of this difference against diene concentration. The corresponding plots are linear and the slope-to-intercept ratio yields $k_q\tau_T(2)$.

In the case of 2,4,6-trimethylacetophenone, we have been unable to reach a definite conclusion regarding the transients involved, in particular regarding the possible role of biradicals. Paraquat experiments, similar to those described for the other substrates, led to weak signals and extrapolated to a lifetime of 300 ns. Sensitization of 1-methylnaphthalene to yield its easily detectable triplet[20] and Stern–Volmer analysis of the data[21] indicate the presence of a triplet with a lifetime of ca. 260 ns. We believe that, in both experiments, we are scavenging the same species (i.e., the triplet state), which most likely does not generate biradicals, or at least biradicals whose behavior would resemble that of the other biradicals examined in this report. Wagner[3] has reported the involvement of a short-lived triplet state in addition to the one detected by us. We do not observe any trapping by paraquat when we add sufficient *cis*-1,3-pentadiene to quench the long-lived triplet state, and, in general, all attempts to trap biradicals derived from the short-lived triplet were unsuccesful; three interpretations are possible: (i) no biradicals are formed; (ii) the biradicals are too short-lived to be trapped (i.e., $\tau_B < 10$ ns); or (iii) the biradicals are formed but are not good electron donors.

Finally, in the case of **1**, **2**, **3**, and **6** we have also examined the quantum yield of biradical formation, Φ_B. The measurements were carried out against γ-methylvalerophenone for which the value of Φ_B can be taken as 1.0.[22a] The plateau absorbance and the values of Φ_B in matched samples are related by eq 8.[18]

$$\frac{A_\infty}{A_\infty{}^s} = \frac{\Phi_B}{\Phi_B{}^s}\frac{k_T}{k_T{}^s}\frac{(\tau_B{}^s)^{-1} + k_T{}^s[PQ^{2+}]}{\tau_B{}^{-1} + k_T[PQ^{2+}]} \quad (8)$$

The superscript "s" refers to γ-methylvalerophenone for which Φ_B, τ_B, and k_T are known.[17] The values of Φ_B obtained in this manner have been included in Table I.

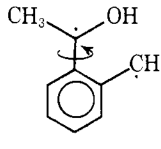
Finally, we note that the concentrations used (typically 0.012 M) are low enough to prevent any self-photoreduction in the case of aldehydes. For example, in the case of tolualdehyde, a 10% yield of photoreduction would require a rate of reaction (triplet attack at the aldehydic hydrogen) of ca. 10^8, considerably faster than typical photoreductions.[22b]

Discussion

The product resulting from abstraction of benzylic hydrogens from the ortho position in the molecules used in our study, or in related molecules, has been described as a biradical or, alternatively, as the triplet state of the enol. In our criteria both nomenclatures describe the same species; in other words, the biradical *is* the triplet state of the corresponding enol. We use the name "biradical" simply because it describes best the properties exhibited in our work.

Findlay and Tchir[7] have raised the question as to whether there should be one or two biradicals, reflecting the number of ground state enols in monosubstituted systems (e.g., **1** and **2**). We find evidence for only one type of biradical in the case of **1**, **2**, **3**, and **6**. Naturally, there is no other possibility in the case of **3** and **6**, while in the case of **1** and **2** it should be taken to mean that bond rotation in **8** and **9** is considerably faster than biradical decay. In the case of **4**, we have recently shown[23] that the formation of two photoenols involves a common intermediate which was assigned to the biradical. Indeed, if full rotational equilibration is achieved in the case of **4**, the same can be expected for all the other systems, involving longer biradical lifetimes and smaller substituents.

The involvement of only one biradical in the photochemistry of **1** and **2** shows that both triplet states decay to yield the same species (i.e., **8** or **9**). These results support Wagner's suggestion[3] that the two biradical precursors are the syn and anti conformers of the triplet state. That is, the syn conformer undergoes fast intramolecular hydrogen transfer, while the anti conformer must undergo bond rotation prior to hydrogen transfer. In systems where alternative reaction paths are not available, the lifetime of the long-lived triplet state [$\tau_T(2)$ in Table I] would be determined by the rate of bond rotation. Two types of experiments can be designed in order to test this mechanism: (i) locking the molecule in one conformation; and (ii) substituting at both sides of the carbonyl chromophore, i.e., using 2,6-dimethylated molecules. The first approach has been successfully used by Wagner,[3] Wirz,[4] and ourselves in the case of substituted tetralones. The second approach has been attempted by Wagner[3] with 2,4,6-trimethylacetophenone and related molecules and it was concluded that "the photokinetics of 2,6-dialkyl ketones remain as uninterpretable as ever", a conclusion which is definitely applicable to our results for **5**. However, we were more successful with mesitylaldehyde, **6**, which showed the expected behavior, that is, only one triplet state which leads to a biradical whose behavior clearly parallels that of the biradical from **2**. It seems reasonable to assume that the unusual and as yet not understood behavior of **5** must be related to the presence of a methyl substituent at the carbonyl group, since the analogous aldehyde shows "normal" (or predictable?) behavior. Wagner's[3] suggestion that the unexpected behavior of triplet **5** is related to the nonplanarity of the 2,4,6-trimethylbenzoyl group in this molecule seems reasonable, although the fact that the short-lived triplet, which is a cyclobutanol precursor, does not yield any efficient electron donor remains unclear.



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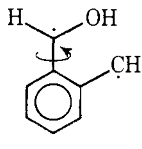

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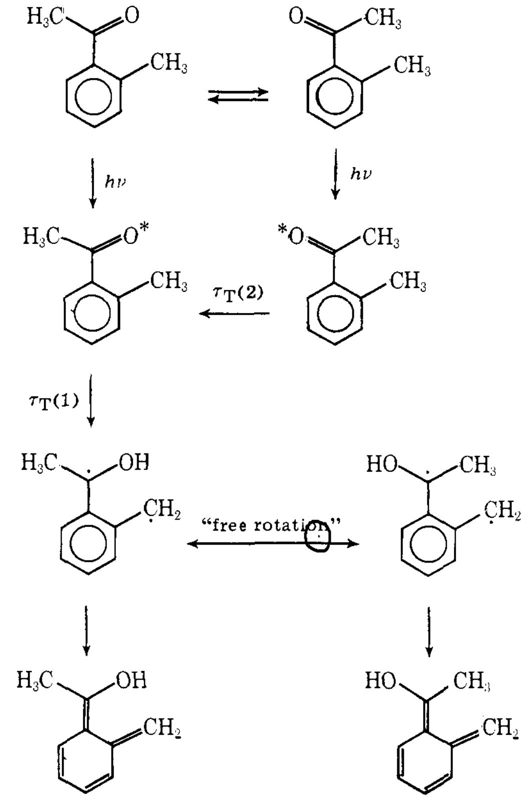
Transient assignments in the photochemistry of **4** have also been the subject of considerable speculation. Uji-Ie et al.[13] have recently proposed that the two ground-state enols arise from two different triplet states via two independent reaction paths. Such a mechanism would require the anti triplet state to be the precursor of the anti enol. We find it difficult to understand how the anti triplet would abstract a hydrogen atom if it does not interconvert to the syn triplet state. Uji-Ie's conclusion[13] is based on the fact that the quenching of the formation of the two enols by naphthalene in the presence of oxygen leads to two different Stern–Volmer slopes, one for each enol. In recent work,[23] we have shown that the conclusion reached by Uji-Ie et al. is incorrect as a result of interference by triplet naphthalene and singlet oxygen, which vitiate the kinetic analysis.

Scheme I



Biradical lifetimes decrease as the possibility of delocalizing the electron from the ketyl radical site increases. If biradical decay involves intersystem crossing, this would have to be faster for those systems with the smaller overlap between the two electron clouds. It is possible that the changes in lifetimes reflect, to some extent, changes in the $^1S-^1T$ gap in the enols.

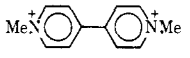
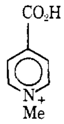
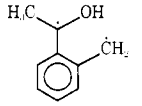
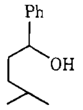
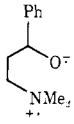
The relative importance of the anti conformation in the triplet state increases with the size of the substituent on the carbonyl group; i.e., the anti conformer accounts for 42% of the triplets in the case of **2** and 27% for **1**. It should be noted that the relative population of the triplet state conformations reflects a combination of the ground-state conformational ratio and the relative efficiencies of intersystem crossing for the two excited singlets (see also eq 7). Bond rotation is too slow to compete with intersystem crossing, which in aromatic ketones occurs in the picosecond time domain.

The tetralone triplet (**3***) is longer lived than the short-lived triplet from *o*-methylacetophenone (see Table I). We believe that the difference reflects the decrease in reactivity resulting from 2,3,6-alkyl substitution, resulting from increased π,π^* character, an effect which has also been observed in other phenyl ketones.[24] Comparison of the triplet lifetimes for **2** and **6** also shows a slight increase. We also find that the aldehyde group is less reactive than the keto group.

Comparison of the long triplet lifetimes [$\tau_T(2)$] for **1** and **2** shows that anti-to-syn interconversion is faster in the case of **1** showing that the anti conformation is unfavorable in this molecule. The same effect is reflected in the syn:anti conformational ratio.

Scheme I shows the mechanism proposed and exemplified in the case of **1**. Conformational equilibrium is achieved in the ground state, while the triplet state, produced via fast intersystem crossing (not shown in the scheme) from the singlet state, decays via hydrogen transfer (syn) or bond rotation followed by hydrogen transfer (anti) to a common biradical. As a result the biradical is always produced initially in a syn conformation, but the barrier to bond rotation is low enough to allow the formation of both enols.

Table II. Rates of Electron Transfer by Biradicals[a]

donor	acceptor	
		
	6.5×10^9	4.9×10^9
	$3.2 \times 10^{9\ b}$	$1.7 \times 10^{8\ b}$
	$4.7 \times 10^{9\ c,d}$	$1.9 \times 10^{9\ c,e}$

[a] At room temperature in $M^{-1}\ s^{-1}$ units in 1:4 water:acetonitrile, unless otherwise indicated. [b] Reference 17. [c] Reference 18. [d] In water at pH 11.1. [e] In 4:1 methanol:water containing 0.1 M sodium hydroxide.

A comparison of k_T values shows that the biradicals produced in photoenolization processes are better electron donors than those produced in the Norrish type II reaction or in related processes, Table II.

Our results and interpretation agree well with recent reports by Wagner,[3] Wirz,[4] and Tchir,[7] particularly in the case of *o*-methylacetophenone, which has now been examined by all these groups and which is probably the only example where all transients have been fully characterized and where the effect of the media on their lifetimes is reasonably well understood. Substituted tetralones have provided considerable insight into the elementary steps involved in photoenolizations.[3,4] Aldehydes (see **2** and **6**) seem to lead to the same type of transient phenomena as *o*-methylacetophenone, and the photochemistry of **6** is not plagued by the complications that make **5** such a difficult system.

Comparison of Φ_B and Φ_{isc} for **1**, **2**, and **6** (see Table I) suggests that intramolecular hydrogen abstraction is essentially the only pathway for triplet decay. The small difference between the two values is quite systematic and most likely reflects systematic errors in the determinations. The lower value of Φ_B for **1** is due to lower Φ_{isc}, not to other reaction pathways.

Recent studies[15] have indicated that photoenolization in polymers can be used to photostabilize these systems. The detailed understanding of the kinetics of the different processes involved in the reaction seems essential if such a possibility is to find practical applications.

Finally, we believe that the electron transfer approach used in this work provides an insight into these reactions different from that available from direct detection studies; in particular, in the case of the biradical it eliminates the problem of transient assignments and allows the evaluation of the quantum yields of biradical formation. The combination of both approaches with the sensitization of 1,3-pentadiene isomerization has led to a detailed understanding in the case of **1** and can potentially lead to a similar understanding in other systems.

Experimental Section

Materials. Acetonitrile was an Aldrich Gold label product and was used as received. Water was triply distilled. Paraquat dichloride was a K & K product and was dissolved in water containing hydrogen chloride and reprecipitated with acetone. 4-Carboxy-1-methylpyridinium chloride (Aldrich) was used as received. *trans*- and *cis*-1,3-pentadiene and 1-methylnaphthalene were Aldrich products.

All carbonyl compounds, with the exception of **3**, were commercial products and were distilled prior to use. In general, the photochemistry of these molecules is not very sensitive to impurities, reflecting the short triplet lifetimes.

5,8-Dimethyltetralone (**3**) was prepared from 4-(2,5-dimethylphenyl)butyric acid by using a procedure similar to that described in the literature for α-tetralone.[25] The crude material was then purified by column chromatography (silica gel using as eluent a 4:1 mixture of petroleum ether and ether) and then recrystallized from petroleum ether; its physical and spectroscopic properties agreed well with those in the literature.[26]

Sample Preparation. The samples (1 mL) were contained in tubes (3 × 7 × 40 mm) made of Suprasil quartz and were deaerated by bubbling oxygen-free argon. Typical substrate concentrations were in the 0.01-0.04 M range.

Laser Photolysis. The samples were excited by using the pulses from a Molectron UV-400 nitrogen laser. Transient absorptions were detected by using an RCA-4840 photomultiplier tube; the signal was then terminated into 93 ohm and into a Tektronix R7912 transient digitizer which, in turn, has been interphased to a PDP 11/55 computer; further details have been given elsewhere.[18,27]

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Enthalpies of Acetolysis of Tricyclo[3.2.1.$0^{1,5}$]octane ([3.2.1]Propellane) and 1,3-Dehydroadamantane

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Abstract: The enthalpies of the addition of acetic acid to the [3.2.1]propellane (**1**) and to 1,3-dehydroadamantane (**3**) to give the corresponding bridgehead acetates have been determined. For liquid **1** reacting with liquid acetic acid to give the liquid acetate, $\Delta H_r = -41.18 \pm 0.24$ kcal/mol, and for solid **3** reacting with liquid acetic acid to give the solid acetate, $\Delta H_r = -43.49 \pm 0.08$ kcal/mol. These data have been combined with the enthalpy of the hypothetical addition of acetic acid across an unstrained carbon-carbon single bond to give the strain-energy release on reaction. The values were 55 kcal/mol for **1** and 57 kcal/mol for **3**. The strain energies of **1** and **3** were obtained by adding the strain energies of the products giving for **1** $E_s = 67$ kcal/mol and for **3** $E_s = 64$ kcal/mol.

The small-ring tricyclic compounds commonly known as "propellanes" are of special interest because of their "inverted" tetrahedral geometry in which all four bonds to a bridgehead carbon lie on one side of a plane through the carbon.[2] The hybridization at the bridgehead carbon is close to sp^2 and the central propellane bond is formed by σ overlap of p orbitals.[3] Some of the small-ring propellanes, such as tricyclo[3.2.1.$0^{1,5}$]octane (**1**), are remarkably reactive toward electrophiles and free radicals,[4] whereas others such as tricyclo[2.2.2.$0^{1,4}$]octane ([2.2.2]propellane) have remarkable thermal lability.[5]

The heats of formation or the strain energies of these compounds would be useful quantities in interpreting the reactivity data. There are difficulties with carrying out oxygen bomb calorimetry with the propellanes because of their reactivity and/or difficulty of preparation.

Since the small-ring propellanes possessing cyclopropane rings are reactive toward electrophiles, the enthalpy change associated with these reactions provides a means for studying their strain energies. Acetolysis is a convenient reaction, and we have found that tricyclo[3.2.1.$0^{1,5}$]octane (**1**)[4] and 1,3-dehydroadamantane (**3**)[6] react almost instantaneously at room temperature. The reactions proceed quantitatively to give a single product.

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