cm^{-1}. The first estimate must be reduced by the Franck-Condon factor of the 0-0 band, about 0.1, so it becomes 0.5 cm^{-1}, and therefore close to the second estimate. These estimates are in accord with the maximum experimental values we have found, about 0.3 cm^{-1}.

The small value of ϵ establishes an upper limit to the rate of excitation transfer between dimer halves of about 10^{10} s^{-1}. This is enough for the molecule to make many vibrations while in the distorted configuration and accounts for the sharp lines observed in the spectra.

V. Conclusions

In this series of papers we have used low- and high-resolution ultraviolet spectroscopy and standard molecular quantum mechanical methods to provide a description of the excited states of the simplest aromatic carboxylic acid. We began by establishing the amount of charge transfer from ring to carboxyl group and other properties of the excited states (part 1).[9] Using MO methods and solvent shifts, we then established the changes in the strengths of H-donor and H-acceptor hydrogen bonds in the excited states (part 2).[1] Luminescence studies in variously H-bonded systems were then used to show how the hidden $^3n\pi$ state could be located (part 3).[10] In the present paper (part 4), the effect of H bonding on the geometry of the excited molecule was studied particularly for the ^1L_b state but also for the ^3L_a state. The trapping of the excitation on one monomer unit was established, and the relationship between the increased H-acceptor strength and the increased basicity of the excited state was pointed out. The spectroscopic evidence also clearly shows why in the triplet state the acidity change is less than in the singlet.

The technique of using single-crystal solid solutions made it possible to do high-resolution spectroscopy in these H-bonded molecules. A certain amount of luck is involved in getting a host-guest combination to work, but it should be possible to apply the method to other H-bonded systems.

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References and Notes

(1) Part 2: J. C. Baum and D. S. McClure, *J. Am. Chem. Soc.*, **101**, 2340 (1979).
(2) E. Vander Donckt, *Prog. React. Kinet.*, **5** (1979).
(3) E. G. Cox, D. W. J. Cruiskshank, and J. A. S. Smith, *Proc. R. Soc. London, Ser. A*, **247**, 1 (1958).
(4) G. A. Sim, J. M. Robertson, and T. H. Goodwin, *Acta Crystallogr.*, **8**, 157 (1955).
(5) J. C. Baum, Ph.D. Thesis, Princeton University, 1974.
(6) J. C. Baum and W. L. Cleveland, to be published. Also, W. L. Cleveland, Ph.D. Thesis, Rutgers University, New Brunswick, N.J., 1974.
(7) G. Herzberg, "Molecular Spectra and Molecular Structure. I. Spectra of Diatomic Molecules", 2nd ed., Van Nostrand-Reinhold, Princeton, N.J., 1950, p. 162.
(8) T. Miyazawa and K. S. Pitzer, *J. Am. Chem. Soc.*, **81**, 74 (1959).
(9) Part 1: J. C. Baum and D. S. McClure, *J. Am. Chem. Soc.*, **101**, 2335 (1979).
(10) Part 3: J. C. Baum, *J. Am. Chem. Soc.*, preceding paper in this issue.

Photochemistry of 1,5-Diaryl-1,5-diketones

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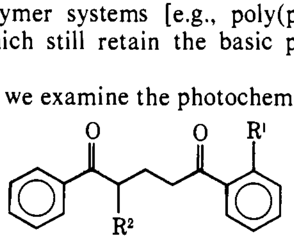
Abstract: The photochemistry of ketones **1-3** has been examined in solution at room temperature by using quantum yield and laser flash photolysis techniques. Triplet energy migration between the two chromophores leads to complete excitation equilibration. In the case of **3**, two triplet states have been characterized, reflecting the syn and anti conformations of the *o*-methylbenzoyl chromophore. The biradicals produced in the triplet decay have lifetimes of ca. 50 ns in wet acetonitrile, for **1** and **2** and 430 ns in the case of **3**, where it results from abstraction of the benzylic hydrogens. Biradicals are produced from **2** with a quantum yield of 1.0; however, the product yields are considerably lower, even in polar hydroxylic solvents. The effect is attributed to strong intramolecular hydrogen bonding in the biradical.

Systems bearing two chromophores of the same type and similar excitation energies are of interest because of the energy migration processes which their photochemistry frequently reflects.[2-4] In particular, several 1,5-diketones have received some attention[5-9] because they can be regarded as the smallest units from polymer systems [e.g., poly(phenyl vinyl ketone)][5,10,11] which still retain the basic properties of the latter.

In this paper we examine the photochemistry of **1-3** with



1, $R^1 = R^2 = H$
2, $R^1 = H; R^2 = CH_3$
3, $R^1 = CH_3; R^2 = H$

the aim of understanding the processes which control the rates and efficiencies of their photocleavage, the migration of the triplet excitation energy between the two chromophores, the role and lifetimes of the biradicals produced by intramolecular hydrogen abstraction, and, in the case of **3**, the importance of photoenolization.

The combination of product studies, quantum yield and quenching experiments, and laser flash photolysis provides a detailed understanding of their photochemistry and elucidates similar photoprocesses in polymers.

Results

Synthesis. Ketones **1-3** were prepared by reaction of the appropriate enamines with vinyl aryl ketones according to reaction 1.

This procedure has been found to give better yields and cleaner products than a direct Friedel-Crafts reaction on the glutaric acid derivative. Products were purified by vacuum distillation, recrystallization, or preparative gas chromatography, as appropriate. In comparison with our earlier experience with other aromatic ketones, we found **1-3** unusually difficult to purify sufficiently to obtain reproducible quantum yields and triplet lifetimes.

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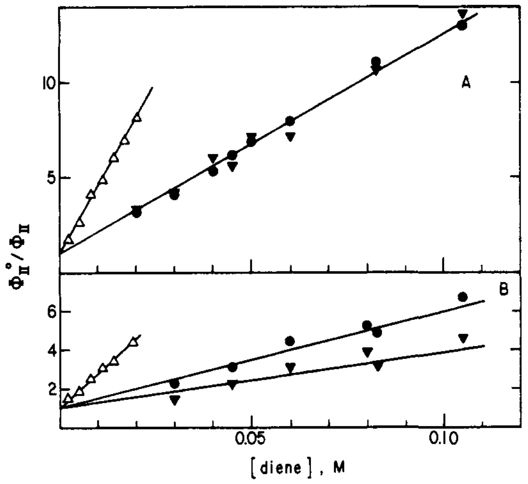
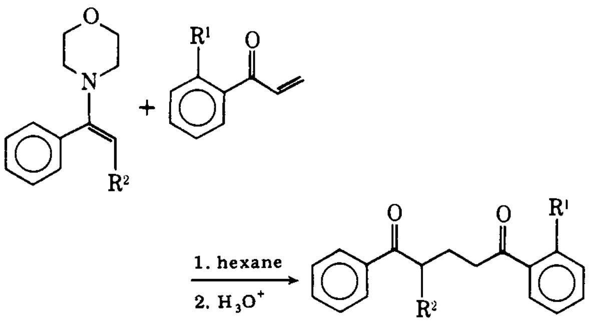


Figure 1. Stern-Volmer plots according to eq 2 in wet acetonitrile (A) and benzene (B), for (●) acetophenone from **2**, (▼) propiophenone from **2**, and (△) acetophenone from **1**.



(1)

Phosphorescence. The phosphorescence spectra of **1** and **2** at 77 K in a methylcyclohexane glass are red shifted by about 12 nm with respect to typical aromatic monoketones. For example, acetophenone and valerophenone have 0-0 bands at 391 and 386 nm, which should be compared with 401 and 402 nm for **1** and **2**, respectively. The result indicates only a weak interaction between the two chromophores.

o-Methylacetophenone phosphorescence under the same conditions is extremely weak and poorly resolved; a similar result was obtained in the case of **3**, indicating that, even at 77 K and in a glass, energy migration leads to a behavior which reflects a property of the *o*-methylbenzoyl chromophore rather than the mixed behavior which would be expected if energy migration was unimportant.

Product Quantum Yields. Reliable quantum yields for **1-3** are difficult to obtain, particularly in the case of **1**. The products of the type II process, phenyl vinyl ketone, or its methyl-substituted derivatives are excellent triplet quenchers.[12] As a result, it becomes essential to work at very low conversions or preferably to extrapolate quantum yields to "zero time", to avoid otherwise important quenching by products which leads to systematically low quantum yield values. Naturally, the same problems arise with samples which have been exposed to light during preparation and handling.

Table I gives the yields (extrapolated to zero conversion) of photofragmentation in several solvents. We note that wet acetonitrile does not lead to limiting quantum yields,[13a] while tri-*n*-propyl phosphate causes a considerable enhancement.[13b] In fact, in the case of **2** the yields of fragmentation products add to 0.87, suggesting that, if cyclobutanols were taken into consideration, the total yields would probably add to one. By contrast, in the case of simple phenyl alkyl ketones, wet acetonitrile is known to be polar enough to cause all the biradicals to proceed to products.[13a]

Table I. Quantum Yields of Photofragmentation[a]

ketone	solvent	Φ_{ACP}[b]	Φ_{PPP}[c]	Φ_{OMACP}[d]
1	benzene	0.18		
1	wet acetonitrile[e]	0.26		
1	benzene/OP(OPr)$_3$[f]	0.52		
2	benzene	0.25	0.10	
2	wet acetonitrile	0.32	0.13	
2	benzene/OP(OPr)$_3$	0.64	0.23	
3	benzene	0.00036		0.00004
3	wet acetonitrile	0.00060		0.00007
3	benzene/OP(OPr)$_3$	0.00087		0.00011

[a] At room temperature. [b] Acetophenone. [c] Propiophenone. [d] *o*-Methylacetophenone. [e] 10:90 water:acetonitrile (v/v). [f] 7% OP(OPr)$_3$.

Table II. Quenching Data in Several Solvents[a]

ketone	solvent	ACP[b]	PPP[c]
1	benzene	185	
1	wet acetonitrile[d]	360	
2	benzene	53	34
2	methanol	117	98
2	wet acetonitrile[d]	114	114
3	benzene	3.8	
3	wet acetonitrile[d]	30	

[a] $k_q\tau_T$ at room temperature, by VPC using 2,5-dimethyl-2,4-hexadiene as a quencher. [b] $k_q\tau_T$ for acetophenone (units of M^{-1}). [c] $k_q\tau_T$ for propiophenone (units of M^{-1}). [d] 10:90 water-acetonitrile (v/v).

We expected to find some cyclobutanols, which are common products in the Norrish type II process.[14,15] Unfortunately, all of our efforts in this direction were fruitless. In the case of **2**, the presence of α-alkyl substitution could be expected to lead to significant cyclobutanol yields;[14,15] unfortunately, it is also expected to lead to six different isomers, all of them photosensitive, due to the presence of both γ hydrogens and relatively weak α-carbon-carbon bonds. Similar difficulties have been previously reported.[6]

Quenching Studies. Triplet lifetimes were obtained from quenching studies using 2,5-dimethyl-2,4-hexadiene as quencher and taking the rate constant for quenching as $1 \times 10^{10}\ M^{-1}\ s^{-1}$ in wet acetonitrile and $5 \times 10^9\ M^{-1}\ s^{-1}$ in benzene.[16] In the case of **1** only one mode of photocleavage is available, while **2** and **3** can fragment in more than one way. Figure 1 shows Stern-Volmer plots according to eq 2 for **1** and **2** in wet acetonitrile (Figure 1A) and for **2** in benzene (Figure 1B).

$$\frac{\Phi^0}{\Phi} = 1 + k_q\tau_T[Q] \qquad (2)$$

Φ^0 and Φ represent the quantum yields for the photofragmentation product (e.g., acetophenone) in the absence and presence of quencher, respectively; k_q is the rate constant for quenching, τ_T is the triplet lifetime, and [Q] the quencher concentration.

In wet acetonitrile, only one Stern-Volmer slope was obtained, even when more than one mode of photocleavage was possible. For example, in the case of **2** the same slope was obtained regardless of whether acetophenone or propiophenone was the product monitored. This would be expected only if complete excitation-equilibration between the two chromophores is achieved.[8]

In the case of **2** in benzene we found that the Stern-Volmer slopes for the quenching of acetophenone and propiophenone production by dienes are different. This difference is outside the range of experimental error (see Figure 1B). Surprisingly, the slope is smaller for propiophenone production, which in-

Table III. Stern-Volmer Slopes from Laser Photolysis Experiments[a]

ketone	solvent	method	$(k_q\tau_T)_1$[b]	$(k_q\tau_T)_2$[b]
1	benzene	1-methylnaphthalene	260	
1	wet acetonitrile	1-methylnaphthalene	340	
3	wet acetonitrile	PQ^{2+}, diene	20	1.7
3	wet acetonitrile	400 nm, diene	19	1.2

[a] At room temperature. [b] In M^{-1} units. The subscript "2" corresponds to the short-lived triplet when more than one is present.

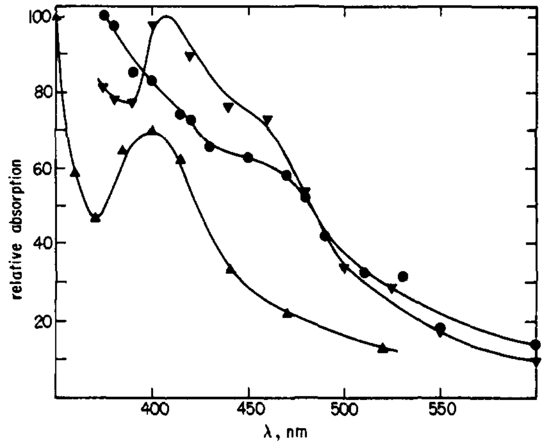


Figure 2. "End-of-pulse" transient spectra observed by irradiation of **1** (●), **2** (▼), and **3** (■) in wet acetonitrile (**1** has been examined in benzene[20]).

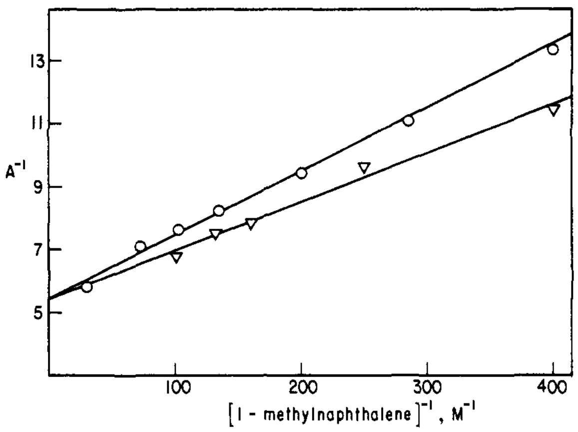


Figure 3. Stern-Volmer plots according to eq 3, obtained using the 1-methylnaphthalene technique (see text) for **1** in benzene (○) and in wet acetonitrile (▽).

volves the abstraction of secondary, rather than tertiary hydrogens. The corresponding $k_q\tau_T$ values are given in Table II. The behavior in methanol was intermediate between benzene and wet acetonitrile.

Quenching of the photofragmentation of **3** in benzene led to $k_q\tau_T \sim 3.8\ M^{-1}$ (based on acetophenone). The formation of *o*-methylacetophenone is also quenched by dienes, but it is difficult to obtain reliable Stern-Volmer slopes, as a result of the low quantum yields involved. We were not able to detect any systematic difference between the quenching of acetophenone and *o*-methylacetophenone, which, within the rather large experimental error, yield equal Stern-Volmer slopes.

Laser Flash Photolysis. Flash experiments were carried out by using the pulses (337.1 nm, 8 ns, ~3 mJ) from a nitrogen laser for excitation. Transient absorptions were monitored by using a detection system with nanosecond response (see Experimental Section). Irradiation of ketones **1-3** in wet acetonitrile leads to the transient absorptions (ca. 10 ns after the peak of the excitation pulse) shown in Figure 2.

The transient absorptions resulting from excitation of **1** decay with reasonable first-order kinetics; however, when we tried to monitor the quenching by dienes, we found that the resulting plots of k_d vs. [diene], where k_d is the experimental first-order decay rate constant, are nonlinear. We believe that this effect is the result of the overlap, in both wavelength and time, of the signals due to the triplet state and the biradical. This effect was observable even at 380 nm where the extinction coefficient of the triplet can be expected to be substantially larger than that for the biradical.[17,18] In fact, the spectrum observed for **1** (see Figure 2) resembles that of the triplet state of aromatic ketones, while that for **2** is quite close to that for the biradical from γ-methylvalerophenone.[17] The transient spectrum recorded in the case of **3** resembles that reported for *o*-methylacetophenone,[19] and should be assigned to the biradical resulting from intramolecular hydrogen abstraction of the benzylic hydrogens.

Triplet lifetimes can be obtained from quenching experiments with 1-methylnaphthalene,[20] which yields its easily detectable triplet.[21] For example, in the case of **1** addition of 1-methylnaphthalene gives the triplet state of the acceptor with yields which follow a Stern-Volmer type of behavior:

$$\frac{1}{A} = \alpha + \frac{\alpha}{k_q\tau_T[Q]} \tag{3}$$

where A is the optical density due to the 1-methylnaphthalene triplet, Q the quencher (1-methylnaphthalene in this case), and α a constant, which is equal to $(\Phi_{isc}I_0\epsilon l)^{-1}$ where I_0 is the absorbed light intensity, Φ_{isc} the quantum yield of intersystem crossing, ϵ the extinction coefficient for naphthalene triplet, and l the optical path. As a whole, α can be regarded as a constant and need not be evaluated explicitly since $k_q\tau_T$ values can be obtained from the intercept-to-slope ratios. It should be noted that these experiments can be regarded as being carried out under true "zero conversion" conditions. The corresponding Stern-Volmer plots for **1** are shown in Figure 3 and the $k_q\tau_T$ values are given in Table III. This technique tends to introduce considerable errors when more than one triplet state is involved,[22,23] or when the substrate leads to significant transient absorptions in the 400-450-nm region.

The 1-methylnaphthalene technique can also be used to measure the quantum yields of intersystem crossing; that is, under conditions of total triplet quenching (achieved directly or by extrapolation), the absorbance due to the naphthalene triplet is proportional to the triplet input. Acetophenone has $\Phi_{isc} \equiv 1.0$ and can be used as a reference substrate. From these studies, we obtained $\Phi_{isc} = 1.0 \pm 0.1$ for **1** and **2** and $\Phi_{isc} = 0.85 \pm 0.2$ for **3**.

Electron Transfer. In earlier publications from this laboratory, we have shown that ketyl sites in biradicals are excellent electron donors.[23-26] Those biradicals produced in the photochemistry of **1-3**, whether in the type II process or as intermediates in the photoenolization reaction, are no exception. Thus, an electron aceptor, A, is reduced to $A^-\cdot$ by reaction with the ketyl site in the biradical, reaction 4.

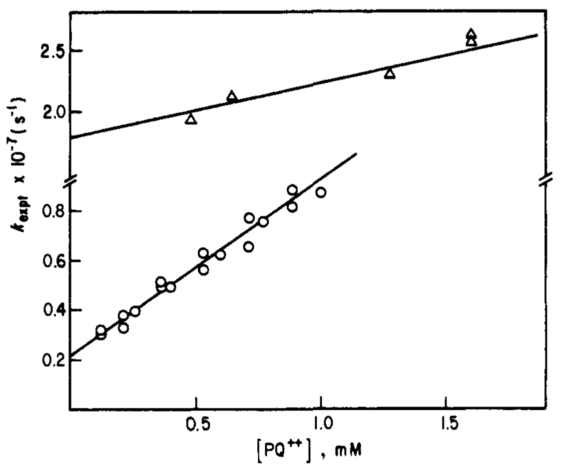
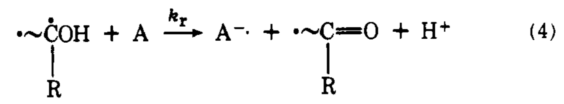
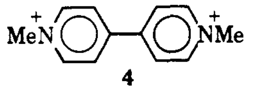


Figure 4. Biradical trapping data according to eq 5 for **2** (△) and **3** (○) in wet acetonitrile.



$$\underset{\displaystyle R}{\cdot\!\sim\!\dot{C}OH} + A \xrightarrow{k_r} A^{-\cdot} + \underset{\displaystyle R}{\cdot\!\sim\!C{=}O} + H^+ \qquad (4)$$

We have used paraquat, **4** (4,4′-dimethyl-1,1′-bipyridylium), as an oxidant, since in earlier experiments with related biradicals it proved to be the best choice for experiments of this type.[24,25]



4

A critical condition that must be fulfilled for the straightforward interpretation[2] of experiments of this type is that the triplet lifetime must be substantially shorter than the biradical lifetime. In general, it is simple to decide whether this criterion is met, from an analysis of results and a comparison with triplet lifetimes measured by other techniques (see above). When the condition of short triplet lifetime is not met, as is the case for **1**, the technique can lead to considerable errors, resulting from kinetic interference or as a result of $PQ^{+\cdot}$ formation via the triplet state of the ketone.

The triplet lifetime can be shortened by addition of triplet quenchers, e.g., dienes,[27] but under these conditions the biradical lifetimes as short as the one obtained here can only be determined by direct detection since addition of PQ^{2+} could conceivably result in triplet diene–paraquat electron transfer processes.[28]

Analysis of the $PQ^{+\cdot}$ buildup traces for biradicals derived from **2** and **3** monitored using laser flash photolysis leads to k_{expt}, the experimental pseudo-first-order rate constant, which depends upon τ_B, the biradical lifetime, and the rate constant of the trapping reaction, k_T, according to eq 5.[24]

$$k_{expt} = \tau_B^{-1} + k_T[A] \qquad (5)$$

Figure 4 shows representative plots of k_{expt} vs. [A]; the corresponding rate parameters are given in Table IV.

In the case of **3**, addition of 0.4 M *cis*-1,3-pentadiene decreases the yield of paraquat radical cations (and therefore of biradicals produced) by 80%. As we will show in the discussion, this value is important in the conformational analysis of **3**.

The quantum yields of biradical formation (included in Table IV) were measured by comparing the "plateau" absorbances in samples containing PQ^{2+} and either γ-methylvalerophenone or one of the ketones under study.[27,29] The values of Φ_B were estimated using eq 6, where the superscript "s" refers to the reference compound (γ-methylvalerophenone) for which $\Phi_B{}^s = 1.0$.[14] A_∞ are the absorbances due to $PQ^{+\cdot}$ in the "plateau" region. These experiments were usually carried out at relatively high concentrations of PQ^{2+} (typically 10^{-3} M) because this minimizes errors caused by uncertainty in the values of τ_B and k_T. These experiments were carried out for **2** and **3** and led to $\Phi_B = 1.0$ and 0.9, respectively. The technique cannot be used accurately for **1** because of the relatively long triplet lifetime, but semiquantitative experiments clearly indicate that Φ_B is of the same order of magnitude as in the case of **2**.

Table IV. Biradical Properties from Laser Experiments[a]

ketone	solvent	$\tau_B{}^b$	$k_T{}^c$	$\Phi_B{}^d$	$\tau_B{}^e$
1	wet acetonitrile				40
2	wet acetonitrile	56	4.2×10^9	1.0	47
2	benzene				27
3	wet acetonitrile	430[f]	6×10^9	0.9	
MVLP[g]	wet acetonitrile	70	2.4×10^9	1.0	76

[a] Room temperature. [b] In nanoseconds from electron transfer studies. [c] In units of $M^{-1}\,s^{-1}$. [d] From eq 6. [e] In nanoseconds from direct detection studies. [f] For the species produced in the photoenolization reaction. [g] γ-Methylvalerophenone; taken from ref 17 and 24.

$$\frac{A_\infty}{A_\infty{}^s} = \frac{\Phi_B}{\Phi_B{}^s}\,\frac{k_T}{k_T{}^s}\,\frac{(\tau_B{}^s)^{-1} + k_T{}^s[PQ^{2+}]}{\tau_B{}^{-1} + k_T[PQ^{2+}]} \qquad (6)$$

When the biradical is considerably longer lived than the triplet state, as is the case for **3**, the values of $k_q\tau_T$ for triplet quenching by dienes, for which we have already described two experimental techniques (see Tables II and III), can also be obtained from the laser induced electron transfer experiments described in this section.[29] To obtain the $k_q\tau_T$ values, a series of samples containing the same concentration of PQ^{2+} and different diene concentrations is examined in order to obtain their "plateau" absorbances (due to $PQ^{+\cdot}$) in the absence ($A_\infty{}^0$) and presence (A_∞) of diene. The data were then fitted by a Stern–Volmer expression, eq 7.

$$\frac{A_\infty{}^0}{A_\infty} = 1 + k_q\tau_T[Q] \qquad (7)$$

The method was applied to ketone **3** in wet acetonitrile, using *cis*-1,3-pentadiene as triplet quencher, and leads to a nonlinear plot, illustrated in Figure 5. The result is indicative of the presence of two distinct triplet states. Proper kinetic analysis[23] leads to $k_q\tau_T = 20\ M^{-1}$ for the long-lived triplet and ca. 1.7 M^{-1} for the short one. The two triplets are produced in a 22:78 ratio (short lived-to-long lived triplet). The technique was not used for ketones **1** and **2** because the comparable triplet and biradical lifetimes could lead to excited state (carbonyl[25,27] or diene[28]) reactions with paraquat.

Biradical Direct Detection Studies. As pointed out above and shown in earlier studies from this laboratory,[17] it is possible to detect directly the biradicals generated in the type II process; their lifetimes can be obtained from the decay of the transient signals under conditions where $\tau_T \ll \tau_B$. The systems can always be "tuned" so that they fulfill this condition by addition of a suitable triplet quencher; obviously, the technique also leads to a substantial decrease in the signal intensity, which in the case of **1** and **2**, particularly the former, must then be overcome by signal averaging. The values of τ_B obtained in this manner have been included in Tables IV and V. In general they are somewhat less accurate than those obtained from the electron transfer experiments, although it should be noted that direct detection has the advantage of not being restricted to systems with short-lived triplets and to polar media.

It is interesting to note that the signal produced upon laser excitation of **3** (shown in Figure 2) can be quenched by dienes,

Table V. Summary of Triplet and Biradical Lifetimes

ketone	solvent	τ_T[a]	τ_B[a]
1	benzene	52	
1	wet acetonitrile	36	40[b]
2	benzene	~9[c]	27[b]
2	methanol	13	
2	wet acetonitrile	11	56,[d] 47[b]
3	benzene	~0.8[e]	
3	wet acetonitrile	2, 0.15	430[d]

[a] In nanoseconds. [b] Direct detection studies. [c] Using the average of two Stern-Volmer slopes; see text. [d] From electron transfer studies. [d] For the product precursor.

that is, the intensity of the signal, but not its lifetime; this is due to the fact that dienes do not quench the observable species (i.e., the biradical), but rather its precursor, the triplet state. This effect follows the same pattern as that discussed above and, indeed, the Stern-Volmer representation (Figure 5) is in full agreement with that obtained from eq 7, except that in this case the "top" absorbances (A^0_{top} and A_{top}) are monitored at 400 nm.[30] Independent treatment of these data yields the parameters given in Table III.

Oxygen Effect. The rate of biradical scavenging by oxygen was obtained from a series of experiments in which the buildup of $PQ^{+}\cdot$ radicals was monitored in samples containing variable concentrations of oxygen, as reported in earlier studies;[31] for **2** we obtained $k_{O_2} = 6.8 \times 10^9$ M^{-1} s^{-1}, a value which is in line with those for similar biradicals.[28,31]

Discussion

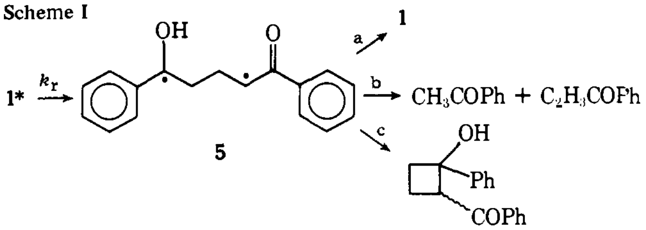
The complexity of the photochemistry of ketones **1-3** clearly parallels the number of reaction paths available. The simplest case is that of **1** where energy migration between chromophores always yields the same excited state and thus excitation transfer is undetectable to our techniques. Triplet decay occurs according to the mechanism of Scheme I, where the asterisk denotes a triplet state.

Consistent $k_q\tau_T$ values for **1** could only be obtained under "zero conversion" conditions. Table V gives a summary of biradical and triplet lifetimes; examination of the values for **1** clearly suggests that the transient absorptions observed by direct irradiation of **1** (see Figure 2) must be due to the overlap of signals from both the triplet state and the biradical. As pointed out in the Results section, the curvature observed in plots representing the quenching of this signal by dienes is consistent with this suggestion. Reports in the literature[5] which are based on the assumption that the signal observed for **1** is due *only* to the triplet state need to be reevaluated, although the rather featureless spectrum obtained from **1** suggests a considerable contribution from the triplet state.[18]

Ketone **2** has two possible modes of photofragmentation, depending on whether the initial hydrogen abstraction occurs at the secondary or tertiary hydrogens; see Scheme II[6,7] where the superscripts in k_r indicate the type of hydrogen atoms abstracted.

The Stern-Volmer slopes in wet acetonitrile are the same for both propiophenone and acetophenone. The rates of hydrogen abstraction of both types of hydrogen are unlikely to be the same; in fact, the shorter triplet lifetime in the case of **2** provides clear evidence for the higher reactivity of the tertiary positions, as expected.[14,15] The agreement between the two Stern-Volmer slopes should be taken to mean that complete equilibration between the two possible excited states has been achieved, eq 8.

Scheme I



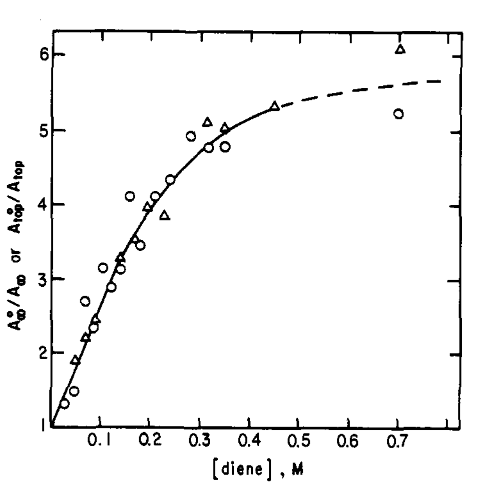
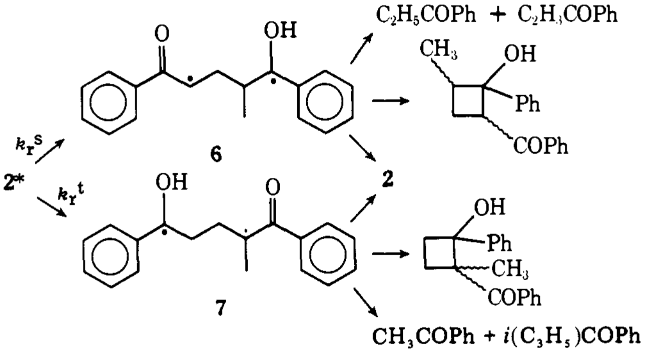
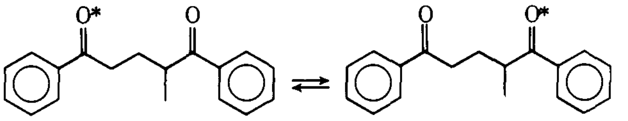


Figure 5. Quenching data according to eq 7 (○) for **3** and similar plot monitoring the "top" absorbances at 400 nm in the absence of PQ^{2+} (△).

Scheme II



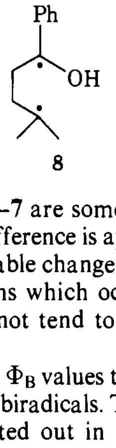


(8)

In other words, the migration of triplet excitation energy between the two chromophores must be faster than the processes by which the triplet state decays. If we assume that the difference in rates must be larger than one order of magnitude, then the frequency of migration between the two chromophores (reaction 8) must excede 10^9 s^{-1}. The result is in agreement with our recent study of copolymers of phenyl vinyl ketone and *o*-tolyl vinyl ketone, where we concluded that the "residence time" of the energy in any given chromophore must be less than 1 ns.[32]

In benzene we have found that the Stern-Volmer slope for acetophenone formation is larger than that for propiophenone. While unexpected, the difference is beyond experimental error. Our results disagree with an earlier report[8] that the two Stern-Volmer slopes are identical.[33] In principle, the effect could be explained, suggesting that the two triplet states are not equilibrated under these conditions and that abstraction of tertiary hydrogen is slower than that of secondary. Not only would this be inconsistent with the well-documented reactivity of these two centers,[14] but it would also disagree with the fact that α methylation causes the triplet lifetime to decrease, as shown by a comparison of the τ_T values for **1** and **2**; further, it seems unlikely that a solvent change would have such a drastic effect on the rate of energy migration. We note that the same difference in slopes was observed with samples of **2** prepared as indicated in the Results section or by Friedel-Crafts synthesis, at different concentrations of **2**, using *cis*-1,3-pentadiene or 2,5-dimethyl-2,4-hexadiene as quenchers and benzene from several sources. Finally, it should be noted that the fact that the quantum yields for acetophenone are substantially higher than those for propiophenone (Table I) indicates that most of the triplets decay via abstraction of tertiary rather than secondary hydrogens. One referee has suggested that biradicals may be reacting with dienes in benzene solution. Quite clearly any mechanism in which the fraction of biradicals yielding products is a function of the quencher concentration can in principle explain the results. Such a mechanism could also explain the relatively short biradical lifetimes measured in the direct technique (using lifetime tuning). While the results are not conclusive in this respect, this possibility is certainly the most attractive one.[34]

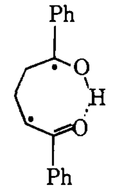
Laser excitation of **2** leads to a transient spectrum (Figure 2) which is largely due to the biradicals **6** and **7**, the triplet state being shorter lived (see Table V). The absorptions due to these biradicals cannot be separated; that is, the spectrum shown in Figure 2 corresponds to a mixture of **6** and **7**. However, the spectra of both components are likely to be almost identical. Except for a small blue shift the spectrum clearly resembles that obtained from γ-methylvalerophenone.[17] The lifetime of 56 ns for the mixture of **6** and **7** compares well with the value of 76 ns for **8**.[24]



8

The values of k_T for **6**–**7** are somewhat higher than those obtained for **8**.[24,25] The difference is apparently real and should be regarded as a considerable change if one takes into account the fact that the reactions which occur with close to diffusion-controlled rates do not tend to be very selective[36] (see Table IV).

Ketones **2** and **3** lead to Φ_B values that are equal to Φ_{isc}; that is, every triplet state gives biradicals. The same is probably true for **1**, although, as pointed out in the Results section, the measurement is more difficult in this case. By contrast, the quantum yields of photofragmentation in wet acetonitrile are rather low, particularly if one takes into account that the biradicals from simple phenyl alkyl ketones usually proceed to products with 100% efficiency in this solvent.[12] That the difference between Φ_{II} and Φ_B is not the result of errors in our Φ_B values is clear from the fact that Φ_{II} can indeed be increased if a better hydrogen bonding reagent is used, for example, trialkyl phosphates.[13,35] In the case of **2**, the fragmentation yields in the presence of tri-*n*-propyl phosphate add to 0.87, which, taking into consideration the rather elusive cyclobutanols, can be regarded as a unity quantum yield for product formation. The question still remains: Why is wet acetonitrile ineffective in causing biradicals **5**, **6**, and **7** to proceed to products quantitatively? In a related example, Lewis[36] has suggested that intramolecular hydrogen bonding can be responsible for this effect; that is, intramolecular hydrogen bonding (see structure **5** below) decreases the effect of an external agent.



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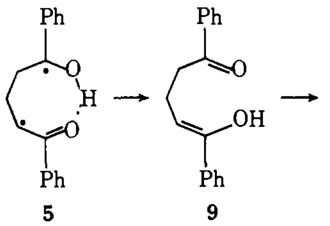
If such an interaction does take place, it could conceivably do more than just compete with the external agent; in fact it could provide a path for the regeneration of the parent ketone, reaction 9.

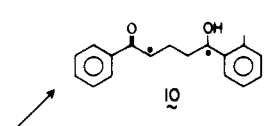


5 **9** (9)

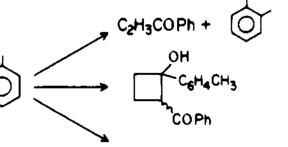
In simple monoketones, the regeneration of the parent ketone is envisioned as a reverse transfer of the hydroxylic hydrogen to the γ position.[14] Reaction 9 involves a 1-7 hydrogen transfer of the same type as that proposed in the reaction of type II biradicals with seleno ketones[37] and oxygen.[27] Unfortunately, our results do not provide a conclusive answer regarding the possible occurrence of reaction 9.

The triplet state of **3** can decay by photoenolization involving the transfer of the benzylic hydrogens,[19,22,23,26] in addition to two different modes of type II photofragmentation, Scheme III.

Biradicals **10**–**12** are all produced, as evidenced by the formation of acetophenone, *o*-methylacetophenone, and the spectral and trapping evidence for **12**. The results of the quenching experiments indicate that **3** has two distinct triplets with lifetimes of 2 and 0.15 ns in wet acetonitrile at room temperature. We propose that these two triplets reflect the syn and anti conformations of the *o*-methyl group with respect to the carbonyl chromophore, structures **3s** and **3a**. This sug-

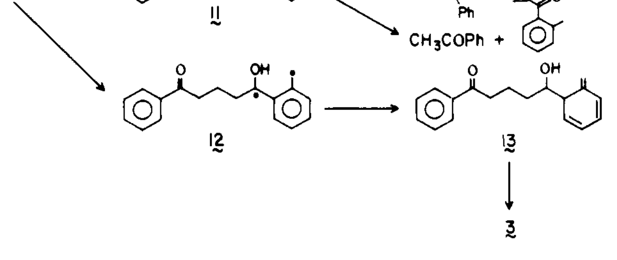


3s

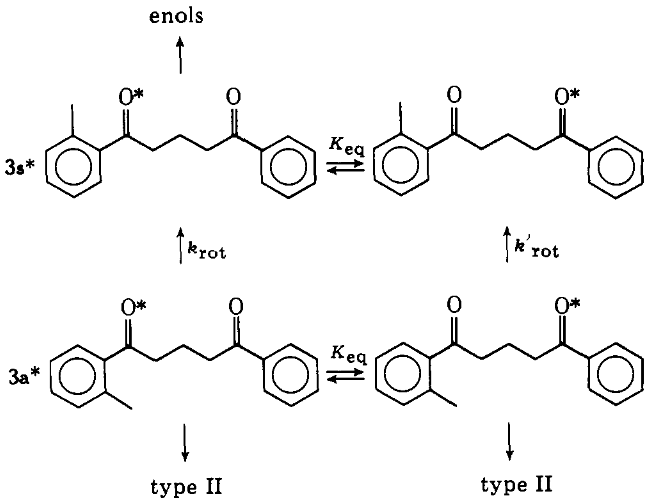


3a

Scheme III



Scheme IV



gestion is consistent with the measurement of only one Stern-Volmer slope from product quenching studies, since both acetophenone and *o*-methylacetophenone can be expected to arise almost exclusively from the anti-triplet conformer. Similar effects are well known in the case of *o*-methylacetophenone and related molecules for which Wagner[22] proposed the same type of conformational control.

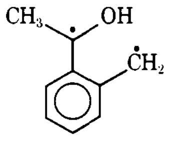
The short triplet lifetime (0.15 ns) corresponds to the syn conformer, while the value of 2 ns should be associated with **3a***, whose lifetime would be controlled by the rate of its interconversion to the reactive state, **3s*** (bond rotation), in addition to chemical decay leading to **10** and **11**. Photoenolization occurs only from the syn conformer and is quite fast from this configuration. For example, only 7% of the photoproducts are formed in the presence of 0.4 M diene, while under those conditions 20% of the photoenolization observed in the nonquenched system takes place. This is due to the fact that essentially *all* the stable photoproducts arise from the anti conformation because the decay of **3s*** leading to **12** is too fast for any of the other reaction paths to compete. The Stern-Volmer slopes for both modes of photofragmentation (Scheme III) and the value measured in the laser experiments for the slow precursor of **12** (Tables II and III and Figure 5) are equal within experimental error, supporting the idea of triplet energy equilibration within each conformation. Perhaps the strongest evidence for efficiency energy migration between the two chromophores is the fact that the quantum yields (Table I) for *both* modes of photofragmentation are quite small. If equilibration within each conformation did not take place, the quantum yields of acetophenone formation would be expected to be "normal", that is, comparable to that for **2** or one-half of the value for **1** (in the 0.1-0.3 range); further, the Stern-Volmer slope for acetophenone from **3** would be expected to be very similar to the value measured for **1** (because of similar substitution); quite clearly this is not the case (see Table II). Scheme IV shows the combination of rotational and energy migration processes taking place in the triplet manifold of **3**; k_{rot} and k'_{rot} are likely to be very similar.

Scheme IV emphasizes the fact that excitation migration is fast enough to reach the equilibrium, while the fast rate of enolization prevents rotational equilibration. The lower yield of *o*-methylacetophenone compared with acetophenone is probably due to an inversion of the n,π^* and π,π^* states in the substituted chromophore which leads to lower reactivity.[14]

A comparison of the total fragmentation yields of **1** and **3** shows that the latter undergoes ca. 0.4% of the photocleavage of **1**. By contrast, poly(*o*-tolyl vinyl ketone) undergoes no detectable photofragmentation.[32a] This difference can be explained by the efficient excitation energy migration through anti conformations of the polymer until an energy sink, the syn conformation, is found.

It is noteworthy that these conformations reflect a combination of ground state geometries and the corresponding intersystem crossing efficiencies, since bond rotation is a slow process in the time scale of singlet lifetimes.[22,23]

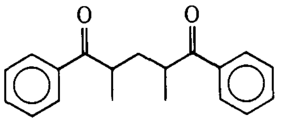
In addition to the quantum yield studies which show that photoenolization is the main reaction path, the results from the laser flash experiments support this conclusion. For example, the transient spectrum from **3** shown in Figure 2 clearly resembles that obtained in the case of *o*-methylacetophenone.[18,19] The lifetime of the biradical derived from **3** should be assigned to **12**, since biradicals of this type are known to be relatively long lived.[26] For example, while the value of τ_T for **8** in wet acetonitrile is 76 ns, that for **14** is 580 ns,[23] which compares well with the value of 430 ns for the biradical from **3**.



14

A comparison of our quantum yield data in benzene for **1** and **2** with studies by other groups shows reasonably good agreement.[6,7]

Our value of τ_T for **2** in benzene of ca. 9 ns seems inconsistent with the value of 70 ns for **15**, reported by Kiwi and Schnabel.[2] We believe that the species observed by these authors was the biradical, not the triplet state of the ketone. The value of 70 ns would seem consistent with this suggestion.[38]



15

Finally, we note that for excitation equilibration to be achieved in the case of **3**, the process of energy migration has to be substantially faster than the sum of the rates of the type II process and bond rotation, which also supports a "residence time" for the excitation in a given chromophore of less than 1 ns.

Conclusion

Energy migration in 1,5-diaryl-1,5-diketones is fast enough to lead to complete equilibration of the excitation between the two chromophores. The frequency of energy hopping must exceed 10^9 s^{-1}. The triplet state decays to give 1,4-biradicals, which when they are not centered on benzylic carbon atoms have lifetimes of ca. 50 ns in wet acetonitrile and are better electron donors than those derived from simple phenyl alkyl ketones. These biradicals are produced with quantum yields close to one; however, the products are formed with quantum yields significantly lower than unity and polar solvents are relatively inefficient in preventing the back reaction of the biradicals to yield the parent ketone. The effect is attributed to strong intramolecular hydrogen bonding.

When the ketone contains ortho benzylic hydrogens (**3**), the main reaction path is the photoenolization of the *o*-methylbenzoyl chromophore. A kinetic study reveals that, while the energy migration equilibrium is reached, the conformational equilibrium (syn-anti) is not. As a result of energy migration, the presence of an *o*-methyl substituent in one of the rings causes a decrease in the yield of *both* modes of type II photocleavage.

Flash excitation of ketones **2** and **3** leads to the detection of the resulting biradical, while in the case of **1** the triplet state is long lived enough that the observable signals correspond to a mixture of both species.

Experimental Section

Materials. Ketones **1**-**3** were prepared from the corresponding enamines according to reaction 1. Typically 2 g of the enamine and an equimolar amount of the corresponding aryl vinyl ketone in 10 mL of hexane were stirred overnight. After removing the hexane, the residue was heated with 10% HCl at room temperature for several hours. The product was extracted into ether and the organic phase dried and concentrated. The samples of **1** and **3** were recrystallized several times from hexane while **2** was distilled. The enamines[40] and aryl vinyl ketones[41,42] were prepared as reported in the literature. The properties of **1** and **2** were in good agreement with those in the literature.[43]

For **1**, we obtained mp 65 °C; IR 1680 s ($C{=}O$, wavenumbers); NMR δ 2.13 (p, 2 H, CH_2), 3.05 (t, 4 H, CH_2CO), 7.1-8.2 (m, 10 H, phenyl). For **2**: bp 185-190 °C (0.8 Torr); IR 1678 s ($C{=}O$); NMR δ 1.21 (d, 3 H, methyl), 2.13 (m, 2 H, CH_2), 3.00 (m, 2 H, CH_2), 3.63 (m, 1 H, CH), 7.1-8.2 (m, 10 H, phenyls). For **3**: mp 50 °C; IR 1684 s ($C{=}O$), NMR δ 2.13 (p, 2 H, CH_2), 2.48 (s, 3 H, methyl), 3.03 (m, 4 H, CH_2CO), 7.2-7.8 (m, 9 H, aromatic).

All solvents were Aldrich Gold Label and were used without further purification. The quenchers, 1-methylnaphthalene, *trans*-1,3-pentadiene, and 2,4-dimethyl-2,4-hexadiene (all Aldrich) were distilled prior to use; *cis*-1,3-pentadiene (Fluka) was used as received. Paraquat dichloride was a K & K product and purified as described previously.[25]

Steady-State Irradiations. They were carried out in a Rayonet reactor fitted with a merry-go-round and 16 RPR-3000 lamps. Unless otherwise indicated, the samples were deaerated with oxygen-free argon; they were contained in matched tubes made of precision bore tubing (i.d. 0.2500 ± 0.0002 in., made of Corning 7740 glass, Lab. Crest Scientific).

Actinometry. Whenever necessary, the photofragmentation of valerophenone in benzene [Φ(acetophenone) = 0.30][44] was used as an actinometer.

Analysis. Products of type II photofragmentation were examined by gas chromatography by using a column of 5% DC-11 silicone oil on Chromosorb W in a Beckman GC-5 instrument equipped with flame ionization detectors.

The quantum yield of intersystem crossing for **2** was confirmed by studying the sensitized isomerization of *cis*-1,3-pentadiene; analyses were carried out on a β,β'-oxidipropionitrile column.

Spectra. UV-vis spectra were recorded on a Cary-219 instrument. A Spex Fluorolog spectrofluorimeter was used in the luminescence studies. NMR spectra were obtained in a Varian A-60 or XL-100 instrument.

Laser Flash Photolysis. The samples were contained in 3 × 7 mm Suprasil cells and were deaerated prior to irradiation. The pulses (337.1 nm, ~3 mJ, 8 ns) from a molectron UV-400 nitrogen laser were used for excitation and were incident on the sample at an angle of ~15° with respect to the monitoring beam. The monitoring system consisted of a pulsed Eimac 150-W xenon lamp, a Bausch & Lomb high intensity monochromator, and an RCA-4840 photomultiplier tube. The response from the detector was terminated into 93 Ω and into an R-7912 Tektronix transient digitizer which in turn was interphased to a PDP 11/55 multiuser computer system, which received the signals, averaged several shots, processed the data, and controlled the experiment.

Transient spectra were obtained by using a flow system which prevented the accumulation of products in the reaction cell. This is particularly important for 1,5-diketones because the vinyl aryl ketones produced in the reaction are very efficient triplet quenchers.

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References and Notes

(1) The research described herein was supported by the Office of Basic Energy Sciences of the Department of Energy. This is Document No. NDRL-1989 from the Notre Dame Radiation Laboratory.

(2) Turro, N. J. *Pure Appl. Chem.* **1977**, *49*, 405-429.

(3) Wagner, P. J.; Nakahira, T. *J. Am. Chem. Soc.* **1973**, *95*, 8474-8475.

(4) Lissi, E. A.; Encina, M. V.; Castañeda, F.; Olea, A. *J. Photochem.* **1978**, *9*, 69-72.

(5) Kiwi, J.; Schnabel, W. *Macromolecules* **1976**, *9*, 468-470.

(6) Casals, P.-F.; Ferard, J.; Ropert, R.; Keravec, M. *Tetrahedron Lett.* **1975**, 3909-3912.

(7) Salvin, R.; Meybeck, J.; Faure, J. *J. Photochem.* **1976/1977**, *6*, 9-16.

(8) Salvin, R.; Meybeck, J. *J. Photochem.* **1977**, *7*, 411-415.

(9) Salvin, R.; Balard, H.; Meybeck, J. *Actual. Chim.* **1975**, *6*, 38.

(10) Faure, J. *Pure Appl. Chem.* **1977**, *49*, 487-494.

(11) The following list includes a few representative references on poly(phenyl vinyl ketone): Lukac, I.; Hrdlovic, P.; Manasek, Z.; Bellus, D. *J. Polym. Sci., A-1* **1971**, *9*, 69. Golemba, F. J.; Guillet, J. E. *Macromolecules* **1972**, *5*, 212. Somersall, A. C.; Dan, E.; Guillet, J. E. *Macromolecules* **1974**, *7*, 233. Kiwi, J.; Schnabel, W. *Macromolecules* **1975**, *8*, 430.

(12) Encinas, M. V.; Funabashi, K.; Scaiano, J. C. *Macromolecules*, **1979**, *12*, 1167-1176.

(13) (a) Wagner, P. J.; Kochevar, I. E.; Kamppainen, A. E. *J. Am. Chem. Soc.* **1972**, *94*, 7489-7494. (b) Scaiano, J. C. *J. Org. Chem.* **1978**, *43*, 568-570.

(14) Wagner, P. J. *Acc. Chem. Res.* **1971**, *4*, 168-177. Scaiano, J. C.; Lissi, E. A.; Encinas, M. V. *Rev. Chem. Interm.* **1978**, *2*, 139-196.

(15) Lewis, F. D.; Hilliard, T. A. *J. Am. Chem. Soc.* **1972**, *94*, 3852-3858.

(16) See, e.g., Grotewold, J.; Soria, D.; Previtali, C. M.; Scaiano, J. C. *J. Photochem.* **1972/1973**, *1*, 471-479, and references therein.

(17) Small, Jr., R. R.; Scaiano, J. C. *Chem. Phys. Lett.* **1977**, *50*, 431-434. *Ibid.* **1978**, *59*, 246-248.

(18) Lutz, H.; Lindqvist, L. *Chem. Commun.* **1971**, 493-494. Lutz, H.; Breheret, E.; Lindqvist, L. *J. Phys. Chem.* **1973**, *77*, 1458-1462; *J. Chem. Soc., Faraday Trans. 1* **1973**, *69*, 2096-2102.

(19) Haag, R.; Wirz, J.; Wagner, P. J. *Helv. Chim. Acta* **1977**, *60*, 2595-2607.

(20) Beck, G.; Dobrowolski, G.; Kiwi, J.; Schnabel, W. *Macromolecules* **1975**, *8*, 9-11.

(21) Porter, G.; Windsor, M. W. *Proc. R. Soc., Ser. A* **1958**, *245*, 238-258.

(22) Wagner, P. J.; Chen, C.-P. *J. Am. Chem. Soc.* **1976**, *98*, 239-241. Wagner, P. J. *Pure Appl. Chem.* **1977**, *49*, 259-270.

(23) Das, P. K.; Encinas, M. V.; Small, Jr., R. D.; Scaiano, J. C. *J. Am. Chem. Soc.* **1979**, *101*, 6965-6970.

(24) Small, Jr., R. D.; Scaiano, J. C. *J. Phys. Chem.* **1977**, *81*, 828-328. *Ibid.* **1977**, *81*, 2126-2131.

(25) Small, Jr., R. D.; Scaiano, J. C. *J. Phys. Chem.* **1978**, *82*, 2662-2664.

(26) Small, Jr., R. D.; Scaiano, J. C. *J. Am. Chem. Soc.* **1977**, *99*, 7113-7114.

(27) Encinas, M. V.; Scaiano, J. C. *J. Am. Chem. Soc.* **1979**, *101*, 2146-2152. Small, Jr., R. D.; Scaiano, J. C. *Ibid.* **1978**, *100*, 4512-4519.

(28) Caldwell, R. A.; Pac, C. *Chem. Phys. Lett.* **1979**, *64*, 303-306.

(29) Encinas, M. V.; Scaiano, J. C. *J. Am. Chem. Soc.* **1978**, *100*, 7108-7109.

(30) The "top" absorbances were measured about 10 ns after the maximum of the excitation pulse; they reflect the biradical signal before significant decay occurs.

(31) Small, Jr., R. D.; Scaiano, J. C. *Chem. Phys. Lett.* **1977**, *48*, 354-357.

(32) (a) Bays, J. P.; Encinas, M. V.; Scaiano, J. C. *Macromolecules* **1979**, *12*, 348-350. (b) Studies completed while this paper was being considered for publication indicated that, in the homopolymer, poly(phenyl vinyl ketone), the frequency of migration is ~10^{12} s^{-1}.[12]

(33) The solvent is not indicated in the original publication,[8] but we presume it is the same as in other studies from the same laboratory, i.e., benzene; further, the value of 68 M^{-1} reported would not be consistent with a polar solvent (see Table II).

(34) While simple biradicals do not react with dienes efficiently,[27] it has been suggested (P. J. Wagner, private communication) that α-keto radicals could behave differently reflecting the increase in electron acceptor ability.

(35) Studies from Wagner's laboratory also confirm that compound 1, when extrapolated to zero conversion in the presence of pyridine, yields products with quantum yields close to unity: P. J. Wagner, private communication.

(36) The reactivity is similar to that of the biradical from γ-phenyl-γ-hydroxybutyrophenone.[24] See also, Lewis, F. D. *J. Am. Chem. Soc.* **1970**, *92*, 5602-5608.

(37) Scaiano, J. C. *J. Am. Chem. Soc.* 1977, *99*, 1494-1498.

(38) The misassignment is not uncommon. Faure et al.[39] have pointed out that the signals which had been previously assigned to the triplet state of poly(phenyl vinyl ketone)[20] were in fact due to the biradical.

(39) Faure, J.; Fouassier, J.-P.; Lougnot, D.-J.; Salvin, R. *Nouv. J. Chim.* **1977**, *1*, 15-24.

(40) Paquette, L. A.; Stucki, H. *J. Org. Chem.* **1966**, *31*, 1232-1235.

(41) Freedman, H. H.; Mason, J. P.; Medalia, A. I. *J. Org. Chem.* **1958**, *23*, 76-82.

(42) Thorsett, E. D.; Stermite, F. R.; O'Donnel, C. M. *Synth. Commun.* 1972, *2*, 375-381.

(43) Merle-Aubry, L.; Merle, Y.; Selegny, E. *C. R. Acad. Sci. Ser. C* 1973, *276*, 249-252.

(44) Wagner, P. J.; Keslo, P. A.; Kemppainen, A. E.; McGrath, J. M.; Schott, H. N.; Zepp, R. G. *J. Am. Chem. Soc.* **1972**, *94*, 7506-7512.