Photochemistry of α-Substituted Cyclohexanones. Chemistry of the Intermediate Type II Biradicals

By **Maria V. Encinas** and **Juan C. Scaiano**,* Radiation Laboratory, University of Notre Dame, Notre Dame, Indiana 46556, U.S.A.

U.v. irradiation of α-alkyl-substituted cyclohexanones bearing γ-hydrogen atoms leads to the generation of 1,4-biradicals *via* the Norrish Type II reaction. Triplet derived biradicals are produced with rather low yields reflecting the occurrence of singlet state processes as well as competition with the Norrish Type I reaction. The biradicals are good electron donors and have lifetimes in the neighbourhood of 1—2 μs in wet acetonitrile. Intramolecular γ-hydrogen abstraction in substituted cycloalkanones is considerably faster than in aliphatic ketones, reflecting lower entropy requirements in the former. A comparison of triplet and Type II biradical yields reveals that the main reaction path of the former is the formation of Type I biradicals.

THE photoreactions of cycloalkanones have attracted the interest of photochemists for a number of years, reflecting the rather rich variety of types of behaviour observed.[1-10] Non-substituted cycloalkanones can undergo α-cleavage (Norrish Type I reaction) or photoreduction.[1,2,9,10] α-Methyl-substituted cyclohexanones and cyclopentanones undergo α-cleavage quite efficiently; the reaction proceeds largely *via* a short-lived triplet state.[2] When the cyclic ketone has α-substituents bearing more than two carbon atoms the Norrish Type II process becomes an important reaction path.[1,2,6] The Scheme illustrates the different types of reactions frequently observed.

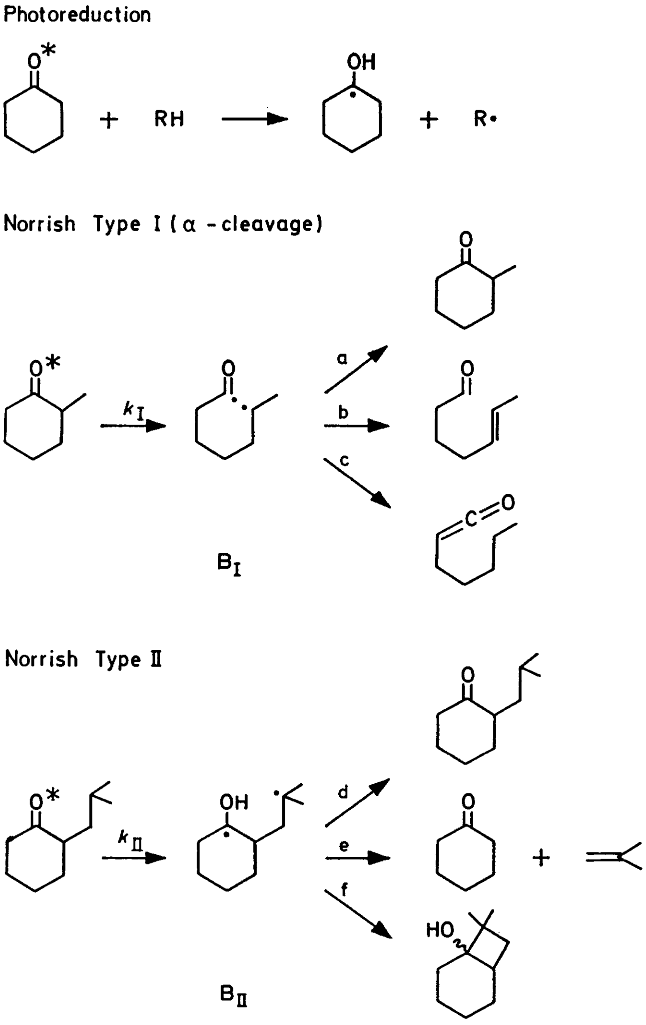
The asterisk denotes a triplet state, though we note that the Type II process, involving the γ-hydrogens in the substituent, occurs from both singlet and triplet states.

The evidence for the presence of biradical intermediates is quite strong. In the case of the Type I process they have been trapped with thiols [4] and nitric oxide [7] and characterized using CIDNP techniques.[10] In the Norrish Type II process there is no direct evidence in the case of substituted cycloalkanones, but the evidence in other types of ketones is conclusive.[11-14]

In principle, the triplet state can decay by any of the processes in the Scheme in addition to radiationless decay. In practice, ketones having α-substituents have very short triplet lifetimes; [1,2] as a result, radiationless decay and photoreduction cannot compete with the Type I and II decays.

Quite frequently the reversal to the parent ketone is the main reaction path for B_I and B_{II}. Quantum-yield techniques cannot differentiate between these two reaction paths; as a result studies of this type can only examine the combined behaviour of both, the excited state and the biradical. In other words, the quantum yields of biradical generation (B_I and B_{II}) cannot be derived from product studies.

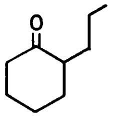
In addition, there have not been any direct studies of biradical lifetimes or reactivities in the case of alkanones. The only reports in the literature refer to the trapping of biradicals from pentan-2-one [15] by hydrogen bromide in the gas phase and their interaction with oxygen for biradicals adsorbed on Vycor glass.[16] In the case of valeraldehyde, we have recently examined the behaviour of the biradicals in solution.[17] While it would be interesting to use the techniques which we have recently developed [13,17] with simple alkanones (*e.g.* hexan-2-one) their absorption spectra does not allow the excitation with the more common laser sources (337.1 nm, nitrogen laser and 347.1 nm, frequency doubled ruby laser). In this paper we take advantage of the red shift of the carbonyl group in cyclohexanones to excite them with a



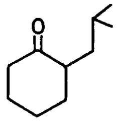
SCHEME

nitrogen laser. The aspects of the photochemistry examined include the quantum yields of photofragmentation and intersystem crossing, the quantum yield of biradical (B_{II}) generation, the triplet and biradical lifetimes and the rates of biradical trapping by 1,1′-dimethyl-4,4′-bipyridylium dications.

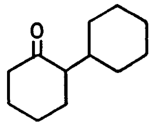
The techniques used include laser flash-photolysis studies of electron-transfer reactions of Type II biradicals, quantum-yield studies, and sensitized isomerization of dienes, all methods which have been widely used in other systems. Four compounds (1)—(4) have been examined; their structures have been chosen so as to change the bond energy of the γ-CH bonds, modify entropy parameters, and introduce resonance stabilization in the γ-position in B_{II}.



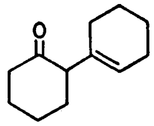
(1)



(2)



(3)



(4)

RESULTS

Steady-state Photolysis.—Quantum-yield studies of Type II photoproducts were carried out by monitoring the formation of cyclohexanone. Yields were measured at room temperature in acetonitrile, a 1 : 9 water–acetonitrile mixture, and cyclohexane; these values are given in Table 1. The contribution of the singlet and triplet states to the photofragmentation yields were determined from quenching plots and extrapolating the yields to high diene concentrations.[18,19] No cyclohexanone was detected even on prolonged irradiation of (4); this is not surprising, since the Norrish Type II photocleavage of (4) would lead to a cyclic allene. Consumption of (4) during irradiation in acetonitrile is low, with $\Phi_{-4} < 0.004$.

TABLE 1

Type II quantum yields [a]

Ketone	Solvent	Φ_{II}	$\Phi_{II}^{triplet}$	$\Phi_{II}^{singlet}$
(1)	Acetonitrile	0.04	0.015	0.025
	Cyclohexane	0.037	0.014	0.023
	Acetonitrile–water [b]	0.038	0.016	0.022
(2)	Acetonitrile	0.04	0.014	0.026
	Cyclohexane	0.04	0.014	0.026
	Acetonitrile–water [b]	0.038	0.015	0.023
(3)	Acetonitrile	0.006	0.002	0.004
	Cyclohexane	0.006	0.002	0.004
	Acetonitrile–water [b]	0.005	0.0015	0.0035
(4)	Acetonitrile–water [b]	~0		

[a] At room temperature, using 300-nm excitation. [b] 9 : 1 (v/v).

The triplet lifetimes were estimated from studies of the sensitized isomerization of *cis*-penta-1,3-diene. Figure 1 shows representative plots of $\Phi_{c\to t}^{-1}$ *versus* [diene]$^{-1}$ from which $k_q\tau_T$, the product of the rate constant for quenching times the triplet lifetime, can be derived [equation (1)[14] where α is an arbitrary constant]. The values of $k_q\tau_T$

$$\frac{1}{\alpha\Phi_{c\to t}} = \frac{1}{\alpha\Phi_{ISC}} + \frac{1}{\alpha\Phi_{ISC}} \cdot \frac{1}{k_q\tau_T} \cdot \frac{1}{[\text{diene}]} \qquad (1)$$

and the corresponding lifetimes obtained taking $k_q = 1.1 \times 10^{10}$ l mol^{-1} (wet acetonitrile) have been included in Table 2.

TABLE 2 [a]

Parameters for reactions of ketones (1)—(4)

Parameter	Units	(1)	(2)	(3)	(4)
$k_q\tau_T$ (isom)	l mol^{-1}	10.3	7.1	1.2	<0.1
$k_q\tau_T$ $(PQ)^{2+}$	l mol^{-1}		5.6		
τ_T [a]	ns	1	0.7	0.1	<0.02
Φ_{ISC}		0.39	0.21	(0.39) [b]	*c*
τ_B (for $B_{,I}$)	ns	2 200	3 000	600	1 200
k_T	l mol^{-1} s^{-1}	3.6×10^9	4.2×10^9	5.5×10^9	2.7×10^9
Φ_B		0.03	0.022	0.02	0.022
k_{II}	s^{-1}	7.7×10^7	1.5×10^8	(5×10^8) [b]	
k_I	s^{-1}	9×10^8	1.2×10^9	(9×10^9) [b]	
P_{II} [d]		0.53	0.68	0.08	

[a] Based on $k_q = 1.1 \times 10^{10}$ l mol^{-1} s^{-1} for dienes in wet acetonitrile. [b] The large error in Φ_{ISC} renders rather unreliable the values of k_I and k_{II}. [c] Triplet lifetime too short to allow any estimation of Φ_{ISC}. [d] Probability of fragmentation for the triplet-derived biradical.

The quantum yields of intersystem crossing were obtained by comparison of the intercepts in Figure 1 with the corresponding intercept for cyclohexanone, used as a standard with $\Phi_{ISC} = 1.0$ (see Table 2).

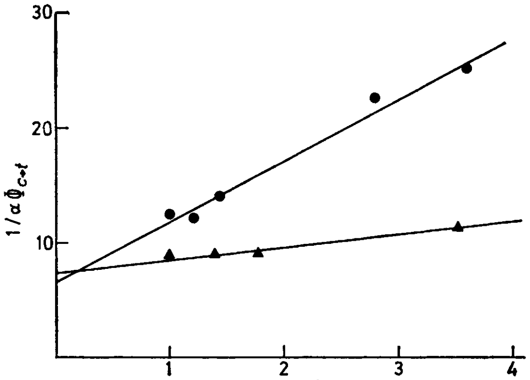
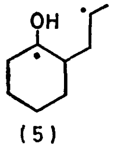
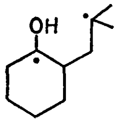


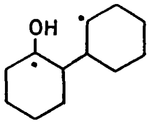
FIGURE 1 Yield of *cis–trans* isomerization of penta-1,3-diene according to equation (1), for (3) (●) and (1) (▲)

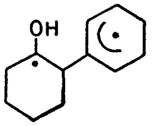
Laser Flash Photolysis.—No transients were observed by 337.1-nm irradiation of solutions of (1)—(4) in wet acetonitrile or n-heptane. Type II biradicals should not be detectable at the wavelengths examined ($\lambda > 350$ nm) if their absorptions are similar to those of the monoradicals.[20] Type I biradicals were not detected; it seems likely that even if they have absorptions in the 500-nm region, similar to those of the acetyl radical,[21] these would be very weak to be detectable under our experimental conditions. Experiments with 2,6-dimethylcyclohexanone were also unsuccessful.

The results described in this section have been obtained in time-resolved studies in which the Type II biradicals (5)—(8) were trapped with paraquat (1,1′-dimethyl-4,4′-bipyridylium, PQ^{2+}) dications.[13, 22]

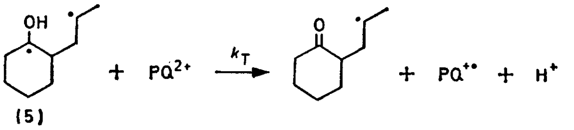

(5)


(6)


(7)


(8)

The technique has been described in considerable detail in earlier papers from this laboratory.[13] Basically, the build up of the radical-cation $PQ^{+\cdot}$, produced by electron transfer from the biradical [illustrated in reaction (2) for (5)] follows pseudo-first-order kinetics and leads to the evaluation of an experimental rate constant k_{exp}, which is related to the rate of trapping k_T and the biradical lifetime τ_B by equation (3).



(5) (2)

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

Figure 2 shows representative plots of k_{exp} *versus* $[PQ^{2+}]$. The corresponding rate parameters have been included in Table 2. We note that the condition of $\tau_T \leqslant \tau_B$, required for the paraquat technique to be applicable, is met by all the systems under study. Further, Type I biradicals (produced from *e.g.* 2,6-dimethylcyclohexanone) do not reduce PQ^{2+}, as expected from the lack of reactivity of acyl radicals.[17]

The signals observed were usually quite weak, with typical plateau absorbances in the neighbourhood of 0.01; these signals made the use of computer-averaging techniques essential. The weakest signals were observed in the case of (3), and as a result all the parameters relating to this ketone and derived from the laser experiments are subject to more error than those for (1), (2), and (4).

The quantum yields of Type II biradical formation can be obtained by comparison of the ' plateau ' (see insert in Figure 2) absorbances in the presence of PQ^{2+} in the system under study and in the case of γ-methylvalerophenone, where Φ_B^s, the quantum yield of biradical formation, is 1.[19] The value of Φ_B given in Table 2 were obtained applying equation (4) to the data.* The superscript s refers to the

$$\frac{A_\infty}{A_\infty^s} = \frac{\Phi_B}{\Phi_B^s}\cdot\frac{k_T}{k_T^s}\cdot\frac{(\tau_B^s)^{-1} + k_T^s[PQ^{2+}]}{\tau_B^{-1} + k_T[PQ^{2+}]} \qquad (4)$$

reference standard, γ-methylvalerophenone, and A_∞ is the absorbance in the ' plateau ' region.

Similarly, a study of the plateau absorbances at constant PQ^{2+} concentration and as a function of added penta-1,3-diene yields $k\tau_q{}_T$ from a conventional Stern–Volmer plot [equation (5)]. The values obtained in the case of (2) and (3) (see Table 2) were consistent with those obtained using the isomerization method, although the latter are subject to rather large errors. A_∞° and A_∞ are the plateau absorbances in the absence and presence of diene, respectively.

$$A_\infty^\circ / A_\infty = 1 + k_q\tau_T[\text{diene}] \qquad (5)$$

The formation of the radical-ions $PQ^{+\cdot}$ can be totally quenched by dienes, suggesting that all the biradicals trapped are triplet-derived. If biradicals are involved in the singlet state photofragmentation they must be extremely short-lived.

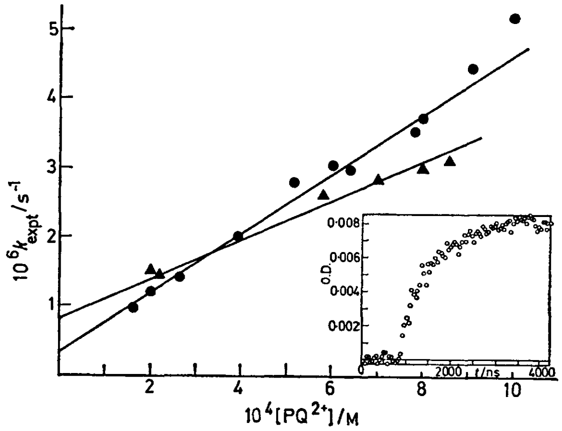


FIGURE 2 Dependence of k_{exp} [equation (3)] upon the concentration of paraquat dications, for (2) (●) and (4) (▲). Insert: typical build-up trace for PQ^{2+} produced by reaction of (5) with 0.000 21M-PQ^{2+}

Finally, from our knowledge of Φ_B, Φ_{ISC}, and τ_T it is possible to calculate the rate of intramolecular hydrogen abstraction according to equation (6). The values obtained have been included in Table 2.

$$k_{II} = \Phi_B/(\Phi_{ISC} \times \tau_T) \qquad (6)$$

DISCUSSION

Though clearly not unexpected, it is probably worth mentioning that our results are the first direct evidence for the intermediacy of Type II biradicals in the photochemistry of alkanones in solution. The lifetimes are substantially longer than those reported for alkyl aryl ketones (*e.g.* γ-methylvalerophenone).[23] Similar effects have been observed in the case of valeraldehyde in solution [17] and pentan-2-one in the gas phase.[15]

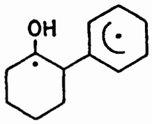
The measurement of Φ_B allows the calculation of the rate of the hydrogen-abstraction step of the Type II process from the lifetime. In the examples considered herein the Type II reaction plays a relatively minor role in the triplet decay process, as shown by the comparison of Φ_B and Φ_{ISC}. Similar conclusions were obtained by Kossanyi *et al.* in the case of 2-propyl-4,4-dimethylcyclohexanone [4] where the value of Φ_B (for B_{II}) was estimated as 0.042.

In view of the short triplet lifetimes, it seems reasonable to assume that for (1)—(3) the rate constant for α-cleavage, k_I, will be given by equation (7). The

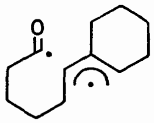
* Unless otherwise indicated the terms biradical and Φ_B refer to the Type II biradical.

corresponding values are given in Table 2. No value of k_I has been estimated for (4) because of the rather large error limits for Φ_{ISC} as well as the possibility of alternative triplet decay mechanisms. The uncertainty in Φ_{ISC} is due to the fact that the short triplet lifetime makes the extrapolation to ' total quenching ' somewhat ambiguous. Radiationless decay from (4*) could also occur *via* reversible intramolecular cycloaddition.[24] In other words, the biradicals (8)—(10) could be expected as possible reaction intermediates. If (9) and (10) are formed at all they must have as their main mode of decay the rearrangement to (4), while (8) does lead to unstable cyclobutanols,[25] but according to our results the quantum yield must be quite low.

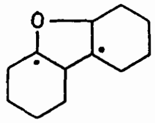
$$k_I = \tau_T^{-1} - k_{II} \qquad (7)$$


(8)

Type II


(9)

Type I


(10)

Cycloaddition

1,3-Shifts, which are common in the photochemistry of many βγ-unsaturated cycloalkanones [8] do not seem to occur with significant quantum yields in the case of (4). Quite clearly, the photochemistry of (4) is dominated by reactions which behave as modes of radiationless deactivation.

We find that the values of P_{II} (the probability of fragmentation) from B_{II} for (5) and (6) are rather high, indicating that product formation is the main reaction path for those biradicals. In the case of (5) and (7), Fleming *et al.*,[6] have shown that the yields of cyclobutanols exceed those of fragmentation products, supporting the conclusion that most biradicals proceed to products, the possible exception being (6). The combined inefficiency of the Type I and Type II processes should be attributed to the low yield of intersystem crossing and the high probability of regeneration of the parent ketone from the Type I (B_I) biradical. The frequent suggestion that the inefficiency of the Type II reaction was due to the requirement to form a high-energy conformation in the transition state is not necessary in the examples considered herein. We note that earlier conclusions regarding the values of k_I and k_{II} or probabilities that the biradicals will follow a certain reaction path cannot be regarded as quantitative since quantum-yield studies cannot differentiate between regeneration of the parent ketone *via* B_I or B_{II}. The absolute measurements of Φ_B reported in this paper overcome this problem.

The rate constants for intramolecular hydrogen abstraction observed (Table 2) are in line with earlier reports on molecules of this type.[1,4,26]

Attempts to trap singlet-derived biradicals were systematically unsuccessful. In the case of triplet-derived biradicals from alkyl aryl ketones, we have proposed that their lifetimes are controlled by intersystem crossing.[13] While the same ideas might apply here, the evidence is not conclusive and the long biradical lifetimes would make an extrapolation from the behaviour in aromatic systems rather speculative.

An alternative explanation for the difference in behaviour between singlet- and triplet-derived biradicals has been offered by Stephenson and Brauman.[27] Their explanation is based on the different initial energy content of the biradicals produced from the two states. We note that since the difference in γ-bond energy between (1) and (4) exceeds the energy gap between the singlet and triplet levels a ' singlet-derived-biradical ' from (1) would have less excess energy than a ' triplet-derived-biradical ' from (4). Nonetheless, *only* triplet-derived biradicals could be trapped. We believe that the energetics of the intramolecular hydrogen abstraction does not play an important role in the solution behaviour of the resulting biradicals.

The values of the Stern–Volmer slope ($k_q\tau_T$) obtained by both techniques, penta-1,3-diene isomerization, and ' plateau ' quenching in the paraquat method agree reasonably well. Since the values of Φ_B are essentially based on the same ideas, the agreement mentioned above suggests that the biradical yields given in Table 2 should be fairly accurate.

Conclusions.—Cyclohexanones bearing α substituents containing γ-hydrogen atoms undergo rapid intramolecular hydrogen abstraction, a process which competes with the major mode of decay, the Type I α-cleavage. Type II biradicals are produced with quantum yields in the neighbourhood of 0.025 and have lifetimes between 0.6 and 2.2 μs in wet acetonitrile at room temperature.

Quantum-yield studies show that product formation is the main reaction path for Type II biradicals and that the overall inefficiency of the photolysis of α-substituted cyclohexanones is largely due to a low yield of intersystem crossing and a high probability of regeneration of the parent ketone by the Type I biradical.

Type II biradicals are excellent electron donors: typical rate constants for electron transfer to paraquat dications are in the 2.5—6 × 10^9 l mol^{-1} s^{-1} range.

EXPERIMENTAL

Materials.—Ketones (1)—(3) (Aldrich) and (4) (Chemical Samples) were all distilled prior to use. Acetonitrile (Aldrich, Gold Label) was used as received. Paraquat dichloride (Aldrich) was purified as previously described.[22] *cis*-Penta-1,3-diene was from K and K.

Steady-state Photolysis.—These experiments were carried out using a merry-go-round fitted in a Rayonet reactor and using sixteen RPR-3000 lamps. The samples (2 ml) were contained in tubes made of precision bore tubing (i.d. 0.2500 ± 0.0002 in; Corning 7740 glass; Lab. Crest Scientific); they were deaerated by argon bubbling when they did not contain pentadiene or by three freeze–pump–thaw cycles to a residual pressure of $<10^{-4}$ Torr when they did. Product analysis were carried out on a Beckman

GC-5 instrument using an Apiezon L or DC-11 Silicone oil column. *cis* : *trans* Ratios for penta-1,3-diene were measured using a Varian 1700 chromatograph and a ββ-oxidipropiononitrile column.

N.m.r. spectra, used to monitor ketone consumption in some experiments, were obtained with a Varian-A60 or XL-100 instrument.

Flash Photolysis.—The instrument makes use of a Molectron UV-400 nitrogen laser for excitation. Further details on the optical system have been given elsewhere.[13, 22, 28]

The small extinction coefficient of the cycloalkanones (1)—(4) at 337.1 nm, combined with low biradical yields usually led to very weak absorptions. Typical ' plateau ' values were in the 0.001—0.010 range, for $PQ^{+\cdot}$ monitored at 398 nm. The signal from the photomultiplier was terminated into 93 ohm and into a Tektronix 7912 transient digitizer. They were then transmitted to a PDP11/55 computer which controlled the experiment and allowed the averaging of signals in the nanosecond time scale. Typically between 30 and 100 shots were averaged to obtain each trace.

This work was supported by the Office of Basic Energy Sciences of the Department of Energy.

[9/142 *Received*, 30*th January*, 1979]

REFERENCES

[1] D. S. Weiss, N. J. Turro, and J. C. Dalton, *Mol. Photochem.*, 1970, **2**, 91; J. C. Dalton, D. M. Pont, D. S. Weiss, F. D. Lewis, and N. J. Turro, *J. Amer. Chem. Soc.*, 1970, **92**, 2564; J. C. Dalton, K. Dawes, N. J. Turro, D. S. Weiss, J. A. Barltrop, and J. D. Coyle, *J. Amer. Chem. Soc.*, 1971, **93**, 7213.

[2] P. J. Wagner and R. W. Spoerke, *J. Amer. Chem. Soc.*, 1969, **91**, 4437.

[3] D. S. Weiss, *Tetrahedron Letters*, 1978, 1039.

[4] B. Guiard, B. Furth, and J. Kossanyi, *Bull. Soc. chim. France*, 1974, 3021.

[5] N. J. Turro and D. M. McDaniel, *J. Amer. Chem. Soc.*, 1970, **92**, 5727; D. R. Morton, E. Lee-Ruff, R. M. Southam, and N. J. Turro, *ibid.*, p. 4349; N. J. Turro and D. R. Morton, *ibid.*, 1971, **93**, 2569; 1973, **95**, 3947.

[6] I. Fleming, A. V. Kemp-Jones, W. E. Long, and E. J. Thomas, *J.C.S. Perkin II*, 1976, 7.

[7] P. Maruthamuthu and J. C. Scaiano, *J. Phys. Chem.*, 1978, **82**, 1588.

[8] K. N. Houk, *Chem. Rev.*, 1976, **76**, 1.

[9] R. Simonaites, C. W. Cowell, and J. N. Pitts, *Tetrahedron Letters*, 1967, 3751.

[10] G. L. Closs, *Adv. Magnetic Resonance*, 1974, **7**, 157.

[11] P. J. Wagner, P. A. Kelso, and R. G. Zepp, *J. Amer. Chem. Soc.*, 1972, **94**, 7480.

[12] R. D. Small, jun., and J. C. Scaiano, *Chem. Phys. Letters*, 1977, **50**, 431.

[13] R. D. Small, jun., and J. C. Scaiano, *J. Phys. Chem.*, 1977, **81**, 828, 2126; *Chem. Phys. Letters*, 1977, **48**, 354; *J. Amer. Chem. Soc.*, 1977, **99**, 7713.

[14] J. C. Scaiano, *J. Amer. Chem. Soc.*, 1977, **99**, 1494.

[15] H. E. O'Neal, R. G. Miller, and R. Gunderson, *J. Amer. Chem. Soc.*, 1974, **96**, 3351.

[16] Y. Kusokawa and M. Anpo, *J. Phys. Chem.*, 1975, **79**, 2225.

[17] M. V. Encinas and J. C. Scaiano, *J. Amer. Chem. Soc.*, 1978, **100**, 7108.

[18] M. V. Encinas and E. A. Lissi, *J. Photochem.*, 1978, **8**, 131.

[19] P. J. Wagner, *Accounts Chem. Res.*, 1971, **4**, 168.

[20] A. Habersbergerova, I. Janovsky, and J. Teply, *Radiation Res. Rev.*, 1968, **1**, 109.

[21] S. Noda, K. Fueki, and Z.-I. Kuri, *J. Phys. Chem.*, 1968, **49**, 3287.

[22] R. D. Small, jun., and J. C. Scaiano, *J. Phys. Chem.*, 1978, **82**, 2662.

[23] R. D. Small, jun., and J. C. Scaiano, *Chem. Phys. Letters*, 1978, **59**, 246.

[24] *E.g.* N. E. Schore and N. J. Turro, *J. Amer. Chem. Soc.*, 1975, **97**, 2482.

[25] R. C. Cookson and N. R. Rogers, *J.C.S. Chem. Comm.*, 1972, 809.

[26] J. C. Scaiano, E. A. Lissi, and M. V. Encina, *Rev. Chem. Interm*, 1978, **2**, 139.

[27] L. M. Stephenson and J. I. Brauman, *J. Amer. Chem. Soc.*, 1971, **93**, 1988.

[28] L. K. Patterson and J. C. Scaiano, to be published.