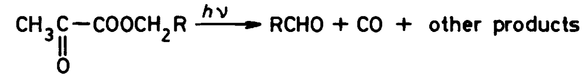
The Mechanism of Photoinduced Fragmentation of Alkyl Pyruvates

By **R. Stephen Davidson** * and **Dean Goodwin**, Department of Chemistry, The City University, Northampton Square, London EC1V 0HB

The finding that t-butyl pyruvate is photostable and has a much longer triplet lifetime than methyl, ethyl, isopropyl, 2-deuterioisopropyl, and benzyl pyruvates, together with triplet quenching studies, shows that alkyl pyruvates fragment from the triplet state *via* a Type II and not a Type I process.

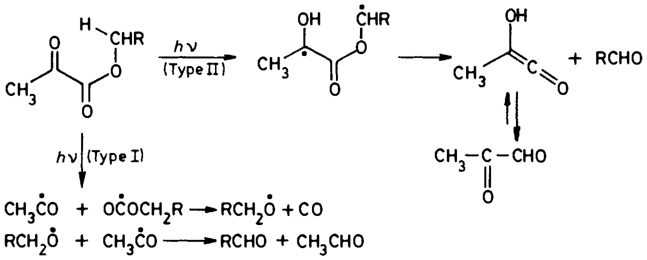
It has been reported that irradiation of alkyl pyruvates in the absence of oxygen leads to fragmentation.[1,2] Two different mechanisms have been proposed to account for the observed oxidation of the alkyl group and are labelled

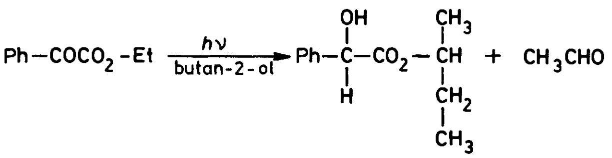


$$CH_3\underset{\underset{O}{\|}}{C}-COOCH_2R \xrightarrow{h\nu} RCHO + CO + \text{other products}$$

Types I[1] and II[3,4] because of their analogy to the fragmentation reaction of ketones.

Leermakers has clearly established that carbon monoxide is produced in the reaction of methyl, ethyl, and isopropyl pyruvates[1] and Binkley has shown that the oxidation of the alkyl group (RCH_2) to give carbonyl compounds occurs in good yield and can be used as part of a sequence of reactions to transform primary and secondary alcohols into carbonyl compounds.[2] There is no direct evidence for the formation of a hydroxyketen in the reaction although the observations that the use of alcohols as solvents for the reaction leads to the formation of esters of lactic acid from pyruvates[4] and mandelic acid from phenylglyoxalates[5] lends credence to their suggested formation.





$$Ph-COCO_2-Et \xrightarrow[\text{butan-2-ol}]{h\nu} Ph-\overset{\overset{OH}{|}}{\underset{\underset{H}{|}}{C}}-CO_2-\overset{\overset{CH_3}{|}}{\underset{\underset{\underset{\underset{CH_3}{|}}{CH_2}}{|}}{CH}} + CH_3CHO$$

The finding by Leermakers that a number of alkyl pyruvates produce acetaldehyde favours the Type I mechanism if the isolated products are primary photochemical products.[1] We now report upon investigations aimed at identifying the mechanism of the fragmentation reaction.

RESULTS

The fragmentation of alkyl pyruvates can be conveniently monitored by ^1H n.m.r. spectroscopy. Samples were therefore irradiated in n.m.r. tubes for known periods of time and their spectra recorded on cessation of illumination. In this way, the formation of formaldehyde, acetaldehyde, propan-2-one, and benzaldehyde from methyl, ethyl, isopropyl, and benzyl pyruvates respectively can be observed and their rates of formation determined (Tables 1 and 2). The addition of a triplet quencher (naphthalene) to the reaction mixture slowed up both the disappearance of the ester and formation of the oxidation product derived from the alkoxy group of the ester. The Stern–Volmer plots deviated from linearity and therefore meaningful quenching rate constants could not be obtained (Figure 1a and b).

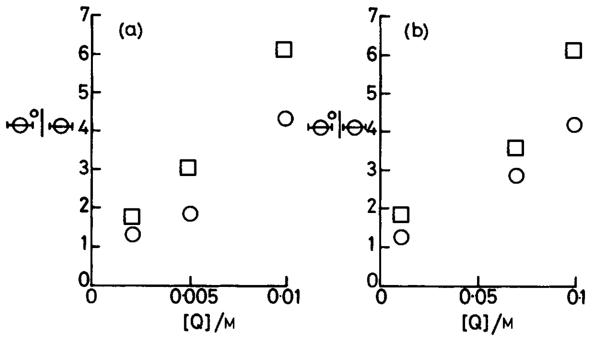


FIGURE 1 (a) Stern–Volmer plot of the quenching of methyl pyruvate (□) and formaldehyde (○) by naphthalene in deuteriated acetonitrile. (b) Stern–Volmer plot of the quenching of isopropyl pyruvate (□) and acetone (○) by naphthalene in deuteriated acetonitrile

The reactions were studied using both deuteriated benzene and deuteriated acetonitrile as solvent. The rate of disappearance was found to be faster in acetonitrile. t-Butyl pyruvate was found to be photostable under similar irradiation conditions. Triplet lifetimes of the esters have been determined using nanosecond laser flash photolysis. The triplet decays obtained from the esters are shown in Figure 2, and the resulting triplet lifetimes are given in Table 3.

DISCUSSION

By following the progress of the reactions by n.m.r. spectroscopy, it soon became apparent that the fragmentation of methyl pyruvate to give formaldehyde is a minor pathway for the destruction of this ester. The yield of formaldehyde based on the amount of ester consumed is very small (*ca.* 12%) (Table 1, CD_3CN–60 min). In contrast, isopropyl pyruvate gives propan-2-

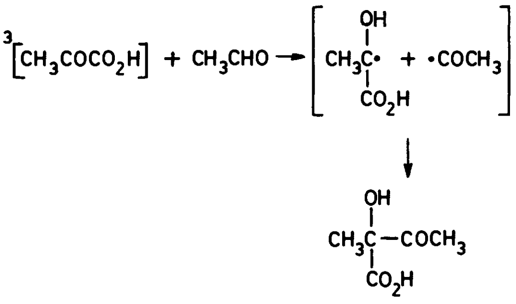
TABLE 1

The photolysis of alkyl pyruvates (0.1M), (A) in degassed solution and (B) in degassed solution containing naphthalene (0.01M), showing the amounts of ester remaining (%) and of carbonyl compound produced (%) after various irradiation times *t*/min

Pyruvate ester (0.1M)	Solvent	(A)						(B)					
		Ester remaining (%)			Carbonyl compound produced (%) †			Ester remaining (%)			Carbonyl compound produced (%) †		
		t 15	*t* 30	*t* 60	*t* 15	*t* 30	*t* 60	*t* 15	*t* 30	*t* 60	*t* 15	*t* 30	*t* 60
Methyl	CD_3CN	54	33	8	15	16	11.5		86	81	*	*	*
Methyl	C_6D_6	86	74	36	7	12	9		85	78	*	*	*
Ethyl	CD_3CN	57	29	5	12	18	24		76	73		4.5	11
Ethyl	C_6D_6	92	73	25	15	30	41		97	80		9	15
		t 30	*t* 60	*t* 90	*t* 30	*t* 60	*t* 90	*t* 30	*t* 60	*t* 90	*t* 30	*t* 60	*t* 90
Isopropyl	CD_3CN	73	67	65	20	26	29	93	84	82	10	13.5	18
Isopropyl	C_6D_6	82.5	67	58	15	23	26	91	80	72	11	19	24
2-Deuterioisopropyl	CD_3CN	62	54	43	23.5	32	37						
2-Deuterioisopropyl	C_6D_6	82	67		15	18	22						
		t 20	*t* 40	*t* 60	*t* 20	*t* 40	*t* 60	*t* 20	*t* 40	*t* 60	*t* 20	*t* 40	*t* 60
Benzyl	CD_3CN		72	68	12	14	19	98.5	94	92		6.7	6.6

* No carbonyl compound observed. † From the alkyl portion of the ester.

one in almost quantitative yield (Table 1). We therefore conclude that the fragmentation of alkyl pyruvates to give carbonyl compounds from the alkyl portion of the molecule is not the only way by which these esters are consumed and that favourability of this reaction increases as the degree of substitution of the alkyl group is increased. It is known that aldehydes react with triplet pyruvic acid [6] and therefore the possibility arises that the aldehydes formed from the methyl, ethyl, and benzyl pyruvates are consumed by reaction with the ester.



$$^3[CH_3COCO_2H] + CH_3CHO \rightarrow \left[CH_3\overset{OH}{\underset{CO_2H}{C}}\cdot + \cdot COCH_3\right] \rightarrow CH_3\overset{OH}{\underset{CO_2H}{C}}-COCH_3$$

TABLE 2

Rate † of photoinduced decomposition of alkyl pyruvates and rate of formation of carbonyl compound in deuteriated benzene and deuteriated acetonitrile (*a*) directly and (*b*) in the presence of triplet quencher (naphthalene)

Pyruvate ester (0.1M)	Solvent	Rate of ester decomposition ($\times$ 10^{-6} mol min^{-1})		Rate of formation of carbonyl compound ($\times$ 10^{-6} mol min^{-1}) ‡	
		a	*b*	*a*	*b*
Methyl	CD_3CN	1.66	0.24	0.48	*
Methyl	C_6D_6	0 43	0.25	0.23	*
Ethyl	CD_3CN	1.29	0.25	0.4	0.07
Ethyl	C_6D_6	0.63	0.18	0.34	0.13
Isopropyl	CD_3CN	0.46	0.15	0.39	0.12
Isopropyl	C_6D_6	0.3	0.16	0.29	0.15
2-Deuterioisopropyl	CD_3CN	0.64		0.4	
2-Deuterioisopropyl	C_6D_6	0.305		0.26	
Benzyl	CD_3CN	0.72	0.083	0.31	0.077

† Rates refer to the first 10% of decomposition of the pyruvate. ‡ From the alkyl portion of the ester. * No carbonyl compound observed.

[a] Rate in neat solvent. [b] Rate with added naphthalene (0.01M).

This probably accounts for the fact that methyl pyruvate is consumed far more rapidly than isopropyl pyruvate. The yield of carbonyl compound produced in the fragmentation reaction, based on the amount of ester used is higher when benzene is used as solvent. The success of the previously described preparative reactions is no doubt due in part, to the use of benzene as solvent.[2] The fact that the rate of disappearance of the ester is slower in benzene than acetonitrile suggests that side reactions, such as reduction, are suppressed in this solvent.* The fragmentation of methyl pyruvate in acetonitrile appears to be particularly complicated. The n.m.r. spectra of the irradiated solution contained a large number of unidentified peaks.

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* We have subsequently found that irradiation of methyl pyruvate solutions containing acetaldehyde leads to consumption of the added aldehyde. The rate of consumption of acetaldehyde is faster in acetonitrile than in benzene, and is drastically reduced in the presence of naphthalene, in each solvent. This indicates that the triplet methyl pyruvate is being reduced by the acetaldehyde, which accounts for the consumption of the aldehyde.

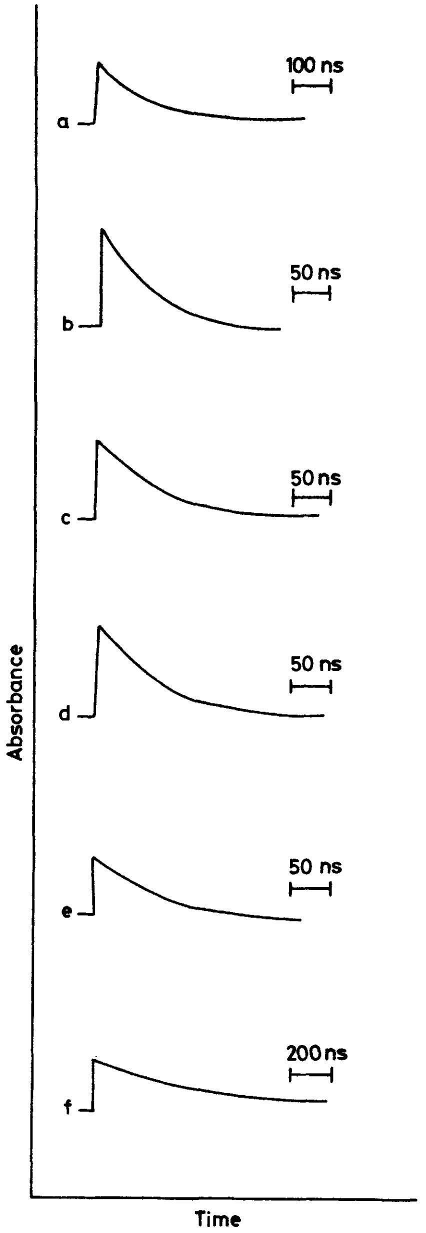


FIGURE 2 Decay of triplet alkyl pyruvates in deoxygenated acetonitrile solution monitored at 685 nm: (a) methyl pyruvate, (b) ethyl pyruvate, (c) isopropyl pyruvate, (d) 2-deuterioisopropyl pyruvate, (e) benzyl pyruvate, and (f) t-butyl pyruvate

The quenching of the fragmentation of the esters and of product formation by naphthalene demonstrates that the triplet state of the ester is involved in these reactions. We have previously shown,[7] by the use of laser flash photolysis, that naphthalene quenches the triplet states of alkyl pyruvates by energy transfer. Scaiano *et al.*[8] have determined, using the same technique, the rate constants for the quenching process and found them to be close to the diffusion-controlled values. Our findings substantiate the earlier claim,[9] which was based on benzophenone sensitisation studies, that the triplet state of the esters is responsible for the fragmentation reaction.

The lack of linearity of the Stern–Volmer plots (Figure 1) was somewhat disappointing as this precluded the extraction of reliable values for rate constants. One of the problems encountered in making the measurements was that in order to obtain measurable amounts of the consumption of the ester and formation of the products, >10% conversion of the starting material had to be allowed. Thus the accumulation of products which may either react (*e.g.* aldehydes) with the triplet ester, or sensitise formation of the triplet ester (*e.g.* propan-2-one will sensitise the formation of triplet isopropyl pyruvate) may well make a simple kinetic analysis of the disappearance of the ester invalid.

If the curvature is real, it could indicate that the naphthalene is quenching more than one excited state of the pyruvate, *e.g.* the singlet and triplet state. However, in our earlier work[10] we have shown that naphthalene does not quench the short-lived excited singlet state of α-keto-esters and this is not surprising when one considers that the excited singlet state of naphthalene is of higher energy than that of the α-keto-ester.

TABLE 3

Triplet lifetimes and rate constants obtained from laser flash photolysis of alkyl pyruvates in deoxygenated acetonitrile solution, monitored at 685 nm

Pyruvate ester	τ/ns	$10^7(\Sigma k_d + k_r)/s^{-1}$	$10^7 k_r/s^{-1}$
Methyl	70	1.43	1.24
Ethyl	60	1.68	1.49
Isopropyl	66	1.52	1.33
2-Deuterioisopropyl	69	1.44	1.25
Benzyl	74	1.36	1.17
t-Butyl	521	0.192	

Another factor which may well account for the non-linearity of the plots is the occurrence of ground state association between the ester and the naphthalene. Association of this type would lead to a ' static ' contribution to the quenching process, and to an overall increase in the efficiency of the quenching process. If one makes drastic assumptions in order to obtain slopes from the Stern–Volmer plots (*e.g.* use only the portion of the graph which covers low concentrations of naphthalene) and consider the triplet quenching process to be truly diffusional, then using a quenching rate constant of *ca.* 1×10^{10} l mol^{-1} s^{-1} the calculated triplet lifetime of methyl pyruvate is *ca.* 40 ns and for isopropyl pyruvate it is *ca.* 4 ns. These values are far shorter than the values obtained by laser flash photolysis. The laser flash photolysis experiments give a direct measure of the triplet lifetime. That the transient observed is the triplet state was shown by the fact that all the esters gave a species having the same absorption spectrum ($\lambda_{max.}$ *ca.* 685 nm in acetonitrile) which decayed with first-order kinetics (Figures 2 and 3) and was quenched by triplet quenchers such as oxygen and naphthalene. The photostable t-butyl pyruvate has a triplet lifetime which is much longer than those of the reactive esters (Table 3).

Using the method developed by Dalton and Turro[11] for determining the rate constants for the Type II reaction of alkanones, it should be possible to use the triplet lifetime of the t-butyl ester to determine the rate constants for reaction of the other esters. The triplet lifetime (τ) of the t-butyl ester is given by equation (1) where

$$\tau = 1/\Sigma k_d \qquad (1)$$

k_d is the sum of the various unimolecular decay processes, *e.g.* radiationless to the ground state, but not including a term for chemical reaction.

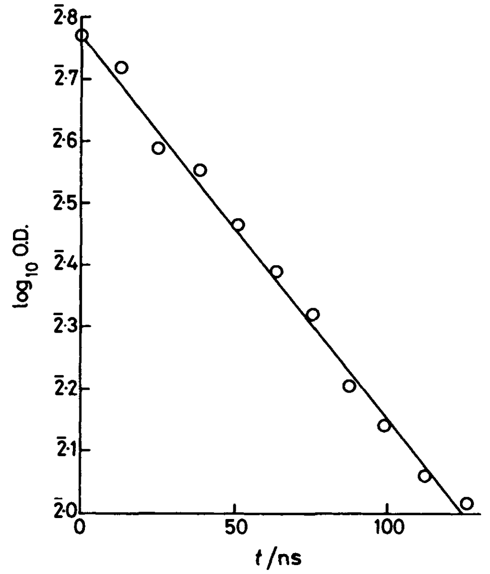


FIGURE 3 Plot of $\log_{10}$ O.D. *versus* time for decay of transient produced from laser flash photolysis of methyl pyruvate, monitored at 685 nm, showing first-order decay kinetics, where k_d = gradient × 2.3026

Substituting the triplet lifetime of the t-butyl ester (evaluated to be 521 ns from the laser flash photolysis study) into equation (1) gives a Σk_d value for this unreactive ester of 0.192×10^7 s^{-1}.

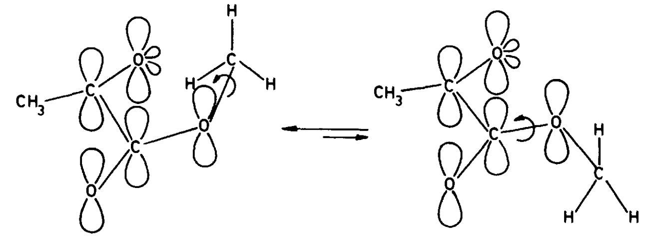
The triplet lifetime (τ') of the reactive esters is given by equation (2) where Σk_d is as above and k_r is the rate

$$\tau' = 1/(\Sigma k_d + k_r) \qquad (2)$$

constant for the Type II reaction of the ester.

Using the Σk_d value for the unreactive t-butyl ester obtained from equation (1) (0.192×10^7 s^{-1}), together with the value of the triplet lifetime (τ') for each of the reactive esters (as determined by laser flash photolysis) and substituting them into equation (2) gives the k_r values for the Type II reaction of the reactive ester (Table 3).

Use of these equations gives k_r values for the methyl and ethyl pyruvates as being 1.2×10^7 and 1.5×10^7 s^{-1}, respectively. The slightly higher reactivity of the ethyl ester is to be anticipated since the abstractable hydrogen atom of the ethyl group is secondary whereas in the methyl group it is primary. However, this rationale predicts that the isopropyl ester should have a higher rate constant than the ethyl ester and this is not found to be the case since the triplet lifetimes of the ethyl and isopropyl esters are similar. If the rate constant for reaction of the ethyl ester had been particularly high, *e.g. ca.* 10^{10} s^{-1} this finding would not have been too surprising since a slight change in C–H bond strength should hardly effect the free energy change for a reaction with such a rate constant. Another puzzling feature is that the triplet lifetimes and quantum yields for photoreaction of the isopropyl and 2-deuterioisopropyl esters are very similar. Our findings that deuteriation has a slight negative primary kinetic isotope effect upon the photoreactivity is in agreement with the results reported by Leermakers.[1] The lack of a positive primary kinetic isotope effect upon the reactivity of the isopropyl ester and the similarity of reactivity between the ethyl and isopropyl esters suggests that the Type II reaction has a very low energy of activation.[11] Certainly the entropy of activation should be almost negligible due to conformations adopted by the ground state of the esters. The *trans–trans* arrangement of the two carbonyl groups[12] means that even for the least favourable conformation (with regard to reaction) only rotation about the oxygen–carbon bond of the oxygen–alkoxy group is necessary to give the ester the correct conformation for the Type II reaction (Figure 4a). This favourable conformation effect should reduce the energy of activation and one would anticipate a high rate constant for these reactions. It is therefore difficult to reconcile the low rate constants for the reactions with the absence of a primary kinetic isotope effect. A similar paradox has been encountered by Coulson and Yang[13] in the photochemistry of hexan-2-one where it was found that replacement of the appropriate hydrogen by deuterium led to a slight *increase* in the quantum yield for the Type II reaction. More surprisingly, the deuterium substitution altered the relative amount of Type II reaction occurring from the excited singlet and triplet states.



a *trans* b *cis*

FIGURE 4 Conformations adopted by alkyl pyruvates

Although we have failed to quantify the parameters for the fragmentation of the alkyl pyruvates, the experimental evidence supports the view that the reaction occurs *via* the Type II process from the excited triplet state.

The finding that the alkyl pyruvates fragment *via* the Type II process begs the question as to how carbon monoxide is produced in these reactions. It has been suggested that this is a secondary product and is derived from methyl glyoxal.[4] A thorough search of our n.m.r.

spectra did not reveal any formation of methyl glyoxal. In a separate experiment methyl glyoxal was found to be unstable under the irradiation conditions used. Apart from the ethyl pyruvate, acetaldehyde, which is the expected product from a Type I process, was not formed. Thus we are unclear as to the eventual fate of the CH_3CO portion of the pyruvate ester.

That alkyl pyruvates do not fragment *via* the Type I process is consistent with the finding that pyruvic acid does not fragment in this way [7] and shows that photolytic cleavage of the bond linking the carbonyl groups in 1,2-dicarbonyl compounds is an unfavourable process.

EXPERIMENTAL

Naphthalene (B.D.H.), methyl pyruvate (Aldrich), ethyl pyruvate (Aldrich), deuteriated benzene (Goss), and deuteriated acetonitrile (Goss) were used as supplied. Isopropyl, 2-deuterioisopropyl, benzyl, and t-butyl pyruvate esters were prepared by the reaction of the appropriate alcohol with pyruvoyl chloride [14] under the experimental conditions previously described.[2] Spectral and physical data confirmed the structures of the prepared esters.

N.m.r. tubes containing the ester solution (10^{-1}M; 0.5 ml) and tetramethylsilane as internal standard, were degassed with a stream of dry argon, stoppered, and rotated within a circular array of fluorescent lamps having a maximum emission at 350 nm (16 × 8W, Sylvania F8T5/BLB). Quenching experiments were performed by the addition of naphthalene (10^{-2}M) to the ester solution. 100 MHz ^{1}H N.m.r. spectra were recorded prior to, and after irradiation. The amount of ester remaining, and the yield of carbonyl compound formed, were evaluated by reference to the ratio of peak heights of the pyruvate methyl singlet and the residual proton peaks of the deuteriated benzene and deuteriated acetonitrile in each case.

Triplet lifetimes were measured using nanosecond laser flash photolysis. An excimer laser (Oxford Lasers Ltd.,) emitting light at an excitation wavelength of 353 nm from a Xe-F gas mixture was the light source. The light pulses produced by this system are of *ca.* 23 ns duration and *ca.* 114 mJ. A conventional pulsed-Xenon arc lamp detection system with a Hamamatsu (Type R 928) photomultiplier tube was used. The transients observed (Figure 2) were found to decay with first-order kinetics and a representative result is shown in Figure 3.

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REFERENCES

[1] P. A. Leermakers, P. C. Warren, and G. F. Vesley, *J. Am. Chem. Soc.*, 1964, **86**, 1768.

[2] R. W. Binkley, *J. Org. Chem.*, 1976, **41**, 3030.

[3] W. M. Horspool in 'Specialist Periodical Report, Photochemistry,' ed. D. Bryce-Smith, The Chemical Society, London, 1978, vol. 9, p. 266.

[4] M. DeBergalis, *Diss. Abstr. Int. B.*, 1979, **40**, 244.

[5] E. S. Huyser and D. C. Neckers, *J. Org. Chem.*, 1964, **29**, 276.

[6] G. L. Closs and R. J. Miller, *J. Am. Chem. Soc.*, 1978, **100**, 3483.

[7] R. S. Davidson, D. Goodwin, and Ph. Fornier de Violet, *Chem. Phys. Lett.*, 1981, **78**, 471.

[8] P. K. Das, M. V. Encinas, and J. C. Scaiano, unpublished results.

[9] G. S. Hammond, P. A. Leermakers, and N. J. Turro, *J. Am. Chem. Soc.*, 1961, **83**, 2395.

[10] R. S. Davidson, D. Goodwin, and Ph. Fornier de Violet, *Tetrahedron Lett.*, 1981, **22**, 2485.

[11] J. C. Dalton and N. J. Turro, *J. Am. Chem. Soc.*, 1971, **93**, 3569.

[12] H. H. Jaffé and M. Orchin, 'Theory and Applications of Ultraviolet Spectroscopy,' Wiley, New York, 1962, p. 419.

[13] D. R. Coulson and N. C. Yang, *J. Am. Chem. Soc.*, 1966, **88**, 4511.

[14] H. C. J. Ottenheijm and J. H. M. de Man, *Synthesis*, 1975, 163.