

LASER FLASH PHOTOLYSIS STUDY OF (*E*)-1-(2'-ARYLIDENE-1'-PHENYLHYDRAZINYL)-1,2-DIBENZOYLALKENES: MECHANISTIC ASPECTS OF PHOTOCHEMICAL RING CLOSURE

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Summary

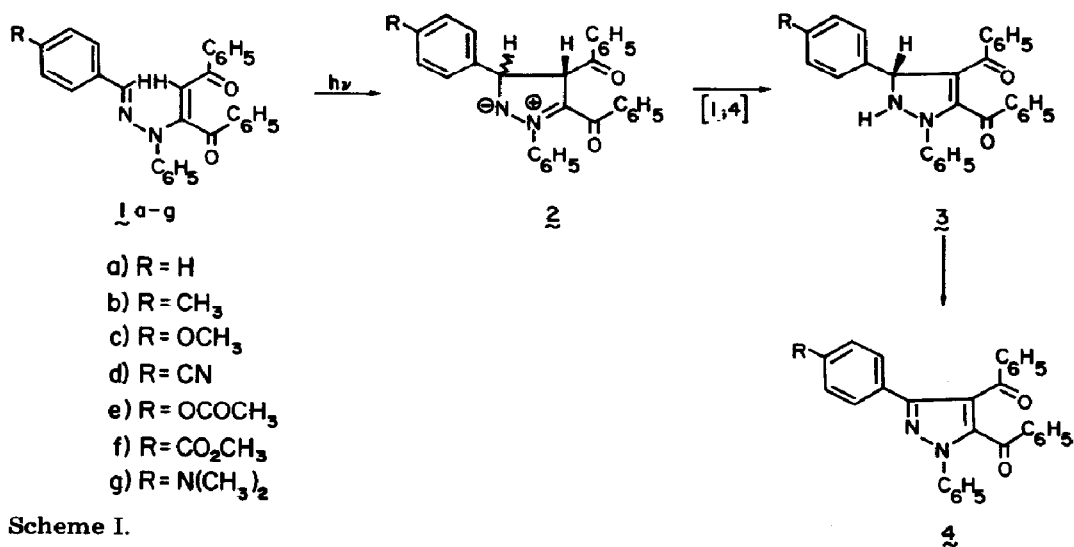
Several (*E*)-1-(2'-arylidene-1'-phenylhydrazinyl)-1,2-dibenzoyl ethylenes, varying from one another in the nature of the *p*-substituent on the 2-benzylidene group, have been studied by nanosecond laser flash photolysis and pulse radiolysis. The transient absorption spectral changes from direct laser excitation ($\lambda_{\text{ex}} = 337.1 \text{ nm}$ or $\lambda_{\text{ex}} = 355 \text{ nm}$) as well as under triplet sensitization by camphorquinone ($\lambda_{\text{ex}} = 485 \text{ nm}$) are explained in terms of the formation of zwitterionic intermediates in the course of intramolecular photocyclization (pentadienyl anion mode) and, in part, by *cis* \rightarrow *trans* isomerization about the ethylenic double bond. From the bleaching of ground state absorption, the lower limits for photochemical loss are estimated to be 0.01 - 0.1 (in benzene and in methanol). The triplets of the dibenzoyl ethylene substrates and the triplet excited states of zwitterionic intermediates are not observed on the nanosecond time scale, presumably because of their short-lived character.

1. Introduction

Besides *cis*-*trans* photoisomerization, *cis*-1,2-dibenzoylalkenes are well known for photoinduced intramolecular phenyl group migration leading to ketene-mediated 2-butenic acids and esters [1 - 6]. More recent studies [7 - 10] have shown that the photochemical pathways of substituted 1,2-dibenzoylalkenes can be strongly dictated by the nature of the substituent. For example, dibenzobarrelenes containing 1,2-dibenzoylalkene moieties undergo the di- π -methane rearrangement (Zimmerman rearrangement [11]), giving rise to dibenzoyl-substituted dibenzosemibullvalenes, and not the 1,2-dibenzoylalkene rearrangement [8, 9]. However, the photoexcitation of 1-pyrazolyl-1,2-dibenzoylalkenes leads to the 1,2-dibenzoylalkene rearrangement as well as electrocyclic reactions involving aryl substituents on the

pyrazolyl ring [10]. In contrast, 1-aziridinyll-1,2-dibenzoylalkenes readily undergo ring expansion to pyrroline derivatives as well as extrusion of alkenes producing nitrene fragments which give isoxazoles via ring closure [12].

In continuation of our interest in the photochemistry of substituted *cis*-1,2-dibenzoylalkenes, we have recently studied several of these systems containing 2'-arylidene-1'-phenylhydrazinyl groups at the 1-position. It has been found [13] that instead of undergoing the usual 1,2-dibenzoylalkene-type rearrangement these substrates under photoexcitation produce five-membered heterocycles through the pentadienyl anion mode of cyclization [14 - 17]. This predominant photochemical pathway, giving 3-aryl-4,5-dibenzoyl-1-phenylpyrazoles as the final major products isolated in high yields (40% - 80%), is described in Scheme I. In this paper, we present some mechanistic aspects of the photocyclization reaction as revealed by time-resolved studies based on nanosecond laser flash photolysis and, to a limited extent, pulse radiolysis. The questions we have addressed in this work concern the spin multiplicity of the photoreactive states, the involvement of zwitterionic intermediates (Scheme I) and evidence for any parallel photo-reaction that may have remained unrecognized in the preparative photochemistry. The substrates under investigation vary in the nature of the substituent on the 2'-arylidene moiety and are shown in Scheme I.



Scheme I.

2. Experimental details

The 1-(2'-arylidene-1'-phenylhydrazinyl)-1,2-dibenzoylalkenes 1a - 1f were prepared through the reaction of appropriate benzaldehyde phenylhydrazones with dibenzoylacetylene. Details of the procedure, yields and physical properties are given elsewhere [13]. The solvents for laser flash photolysis and pulse radiolysis were of Aldrich Gold Label quality. The

sources and methods of purification of compounds used as reagents are described in previous papers from the Radiation Laboratory [7 - 10, 12, 18 - 20].

For most of the laser flash photolysis experiments, use was made of pulse excitation at 337.1 nm (2 - 3 mJ, about 8 ns, Molectron UV-400 nitrogen laser source) in a computer-controlled set-up. Laser pulses at 355 nm (10 mJ or less, about 6 ns) and 485 nm (4 - 6 mJ, about 6 ns) obtained from Quanta-Ray DCR-1 Nd-YAG and PDL-1 dye laser sources were also used in some of the experiments. The system is fully interfaced with an LSI 11 microprocessor which controls the experiment, averages signals and processes the data. The storage and further processing of data were performed in a time-shared PDP 11/55 system. Details of the kinetic spectrophotometer, signal processing and experimental procedures are given elsewhere [18 - 20].

For pulse radiolysis, use has been made of a computer-controlled apparatus, which allows determination of transient absorption spectra at various times (nanosecond to second) after the electron pulse and kinetic measurements of the spectral changes. The pulse electron source was the Notre Dame 7 MeV ARCO LP-7 linear accelerator. A description of the set-up is available elsewhere [21, 22]. To study absorption spectral changes from steady state photolysis, the irradiation was carried out in 1 cm × 1 cm quartz cells with optically flat surfaces. For 366 nm excitation, a set-up consisting of a medium pressure mercury lamp (Bausch and Lomb SP-200) and a monochromator (Bausch and Lomb 33-86-07) was used. The source of 485 nm excitation was a xenon lamp (Eimac 450 W) coupled with a monochromator (Bausch and Lomb 33-86-07). The ground state absorption spectra of the substrates and the photoproducts from steady state photolysis were recorded in a Cary 219 spectrophotometer (1 nm bandpass). For proton nuclear magnetic resonance (¹H NMR) spectra, use was made of a Nicolet NB-300 NMR spectrometer.

3. Results and discussion

Each of the dibenzoylalkene derivatives 1a - 1f is characterized by a moderately strong absorption band system at 320 - 420 nm ($\lambda_{\text{max}} = 370 - 382$ nm, $\epsilon_{\text{max}} = (3.4 - 4.5) \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$ in benzene). Compared with 1a - 1f, 1g has its absorption maximum considerably red shifted ($\lambda_{\text{max}} = 404$ nm, $\epsilon_{\text{max}} = 4.2 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$ in benzene). As a matter of fact, both electron-donating (*e.g.* OCH₃ and N(CH₃)₂) and electron-withdrawing (*e.g.* CN and COOCH₃) groups at the *p*-position of the 2'-benzylidene moiety cause red shifts in λ_{max} , suggesting non-negligible electronic interaction between the enehydrazine and dibenzoylalkene chromophores. On going from benzene to methanol, the absorption maxima move slightly to longer wavelengths (shifts, 1 - 10 nm). Because of the strong ground state absorptions at 337.1 and 355 nm, it was feasible to carry out flash photolysis experiments on dilute solutions (typically 0.1 mM) using direct laser excitation at these

wavelengths. Also, from the onsets of lowest-energy absorption band systems, the lowest singlet energies E_S are estimated to be at 70 kcal mol⁻¹ or lower. Since the singlet-triplet energy separations [23] of typical π - π^* transitions are at least 25 kcal mol⁻¹, the lowest triplet energies of the dibenzoylalkene derivatives can be reasonably located at 50 kcal mol⁻¹ or lower. This consideration is important in the selection of an appropriate triplet sensitizer for sensitization experiments (see below).

The major change upon laser flash photolysis (337.1 or 355 nm) of 1a - 1g in benzene or methanol is the bleaching of the ground state absorption at 320 - 450 nm. This is illustrated in Fig. 1 with 1a as the substrate. Beyond and below the spectral region of ground state depletion, small positive absorbance changes due to photoproducts are observed (Fig. 1). The monitoring of the photoproduct absorptions at the longest time scale (about 150 μ s) shows very little (15% or less) or no decay. The presence of oxygen (about 2 mM) in the solutions does not affect the yields or decay kinetics of the photoproducts. Also, attempts to quench them by di-*tert*-butyl nitroxide

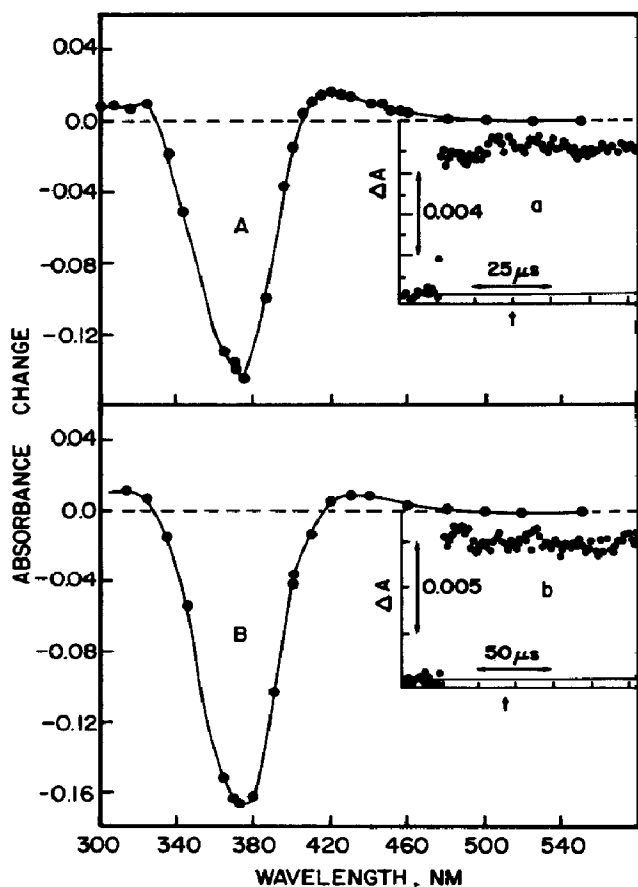


Fig. 1. Absorption changes at 3 μ s following 355 nm laser flash photolysis of 0.05 mM 1a in (A) benzene and (B) methanol. Representative kinetic traces at 425 nm in benzene and at 420 nm in methanol are shown in insets a and b respectively.

radical and ferrocene were unsuccessful ($k_q < 10^6 \text{ M}^{-1} \text{ s}^{-1}$). Based on this, the observed transient absorbances cannot be partially or totally due to the triplets of the dibenzoylalkene derivatives.

Employing benzophenone triplet formation (in benzene) for actinometry, we estimated the lower limits of photochemical yields ($\phi_{\text{PC}}^{\text{lim}}$) from the bleaching of the ground state absorptions. In these experiments, the end-of-pulse absorbance change $\Delta A_{\text{BP}}^{\text{T}}$ due to benzophenone triplet at 532 nm was compared with the negative absorbance changes $\Delta A_{\text{G}}^{\text{S}}$ at 378 nm resulting from photochemical loss of the substrates under 337.1 or 355 nm laser excitation. The selection of 378 nm as the wavelength for monitoring ground state depletion was dictated by the availability of an appropriate interference filter (Oriel 5366) with the transmittance centered at this wavelength. The solutions were optically matched (absorbance, 0.1 in 2 mm cell) at the laser wavelength. $\phi_{\text{PC}}^{\text{lim}}$ was calculated using the equation

$$\phi_{\text{PC}}^{\text{lim}} = \phi_{\text{T}} \frac{\epsilon_{\text{BP}}^{\text{T}} - \Delta A_{\text{G}}^{\text{S}}}{\epsilon_{\text{G}}^{\text{S}} \Delta A_{\text{BP}}^{\text{T}}}$$

where $\epsilon_{\text{BP}}^{\text{T}}$ is the extinction coefficient of benzophenone triplet ($7.6 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$ at 532 nm in benzene [24]), ϕ_{T} is its quantum yield (taken to be unity) and $\epsilon_{\text{G}}^{\text{S}}$ is the substrate ground state extinction coefficient at 378 nm. Since the extinction coefficients of the photoproducts are not necessarily negligible at 378 nm, the quantum yields obtained from eqn. (1) represent the lower limits. The data concerning photoproduct absorption maxima and quantum yields are compiled in Table 1. Note that the wavelength maxima in Table 1 correspond to *difference* absorption spectra and do not necessarily represent the true maxima of the photoproducts.

In order to shed light on the triplets of the dibenzoylalkene derivatives under examination, laser flash photolysis and pulse radiolysis experiments were carried out with camphorquinone (CQ, $E_{\text{T}} = 52 \text{ kcal mol}^{-1}$ [25]), biphenyl ($E_{\text{T}} = 66 \text{ kcal mol}^{-1}$ [26]) and 1-methylnaphthalene (MN, $E_{\text{T}} =$

TABLE 1

Wavelength maxima of absorption spectral changes and lower limits of photochemical yields in the course of 337.1 nm laser flash photolysis of 1-(2'-arylidene-1'-phenylhydrazinyl)-1,2-dibenzoylalkenes

Substrate	Substituent (R)	$\lambda_{\text{max}}^{\text{diff}}$ (nm)		$\phi_{\text{PC}}^{\text{lim}}$	
		Benzene	Methanol	Benzene	Methanol
1a	H	415	425	0.07	0.1
1b	CH ₃	410	430	0.07	0.09
1c	OCH ₃	425	440	0.09	0.08
1d	CN	415	420	0.05	0.07
1e	OCOCH ₃	415	420	0.08	0.06
1f	CO ₂ CH ₃	420	420	0.06	0.08
1g	N(CH ₃) ₂	460	~ 500	0.04	0.01

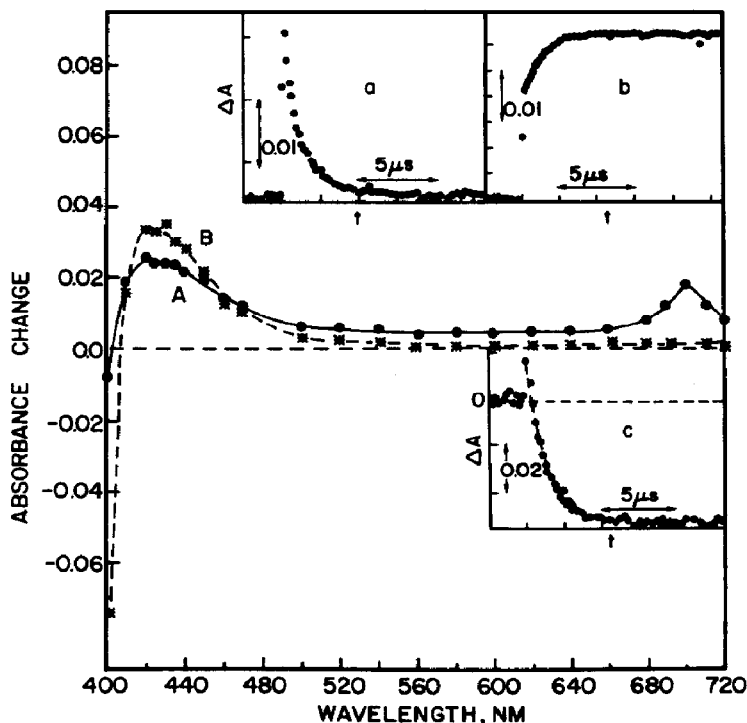


Fig. 2. Absorption changes (A) 0.05 μs and (B) 12 μs following 485 nm laser flash photolysis of about 0.02 M CQ in the presence of 0.5 mM 1c in benzene. Kinetic traces at 700 nm, 425 nm and 400 nm are shown in the insets a, b and c respectively.

60 kcal mol⁻¹ [26]) as triplet sensitizers. Substrates 1a, 1c and 1d were used as acceptors. CQ was directly excited at the laser wavelength 485 nm and its triplet (³CQ*) was monitored from the transient absorption at long wavelength (700 nm) [27]. At the laser excitation wavelength (485 nm), the ground state absorptions of the substrates were negligible at the concentrations used (0.5 - 2 mM). Figure 2 shows representative transient absorption spectra and kinetic traces obtained with 1c as the acceptor. Concomitant with the decay of ³CQ* at 700 nm, the formation of long-lived photoproduct(s) is observed at 410 - 500 nm. From the dependence of the pseudo-first-order rate constant for ³CQ* decay on substrate concentration, the bimolecular rate constants for the quenching of ³CQ* by 1a, 1c and 1d are estimated at $(2 - 3) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ (in benzene). In comparison, the observation ($\lambda_{\text{ex}} = 485 \text{ nm}$) of *N*-methylthioacridone triplet ($\lambda_{\text{max}}^{\text{T}} = 520 \text{ nm}$ [28]) in a benzene solution saturated with 1a, 1c or 1d shows that the thioketone triplet decay is affected very little by these substrates ($k_{\text{q}}^{\text{T}} < 5 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$). Since the triplet energy of *N*-methylthioacridone is located at 42.9 kcal mol⁻¹ [29], it is concluded that the E_{T} of the dibenzoylalkenes under examination are bracketted by 43 and 52 kcal mol⁻¹ (the latter being E_{T} of CQ).

In the triplet sensitization experiment using ³CQ*, at all substrate concentrations (up to 4 mM), the kinetics of the growth of photoproduct absorptions at 410 - 500 nm match very well those of ³CQ* decay at 700 nm.

Even at the highest substrate concentration, no relative lag is noticed in the growth of photoproducts. This strongly suggests that the triplets of 1a, 1c and 1d are too short lived ($\tau < 50$ ns) to make their intermediacy recognized in the formation kinetics of photoproducts.

The decay of the photoproducts (410 - 500 nm), formed under 485 nm laser excitation of CQ in benzene solution saturated with 1a, 1c or 1d, occurs very slowly over microseconds ($\tau_{1/2} > 100$ μ s). The decay kinetics are complex. On a relatively short time scale (about 10 μ s), in some cases, a weak first-order component ($\tau = 4 - 8$ μ s) is noticeable at 460 - 480 nm. This component is slightly oxygen sensitive, as shown by experiments in air-saturated solutions ($k_{q, O_2} \leq 5 \times 10^8$ $M^{-1} s^{-1}$). Unfortunately, the weak character of the short-lived transient absorption does not permit any reliable quenching studies to be carried out.

Triplet sensitization studies were also carried out using, as donors, biphenyl and MN triplets generated by pulse radiolysis [24, 30] in benzene. In a typical experiment, a benzene solution of biphenyl (0.05 - 0.1 M) and a substrate (about 1 mM) was subjected to irradiation by an electron pulse (for about 5 ns). Biphenyl, being at a much higher concentration than the substrate, first accepts energy from the pulse-radiolytic, short-lived solvent triplet ($\tau_T = 3.4$ ns [24]); the resultant, long-lived biphenyl triplet ($\tau_T > 20$ μ s) then transfers energy to the substrate and triplet-mediated photoproducts from the latter are observed. The transient spectra, shown for 1a and 1c in Fig. 3, and the decay kinetics of the photoproducts are found to be very similar to those observed under laser flash photolysis (direct excitation as well as $^3CQ^*$ sensitization, *vide supra*). The absorption due to biphenyl triplet at 350 - 400 nm was not accessible in these experiments because of its strong spectral overlap with the ground state absorptions of

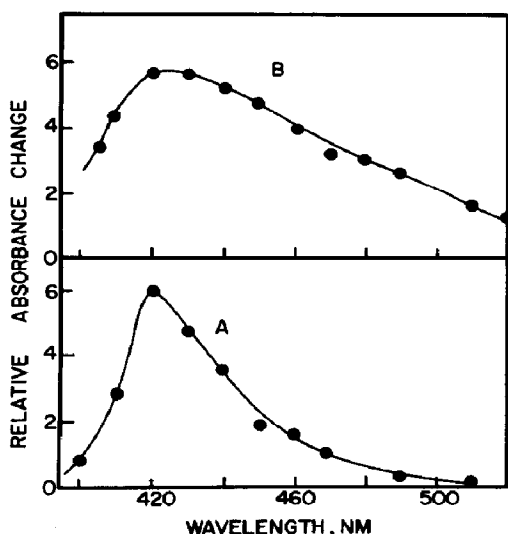


Fig. 3. Absorption changes at 5 μ s following pulse radiolysis of 0.05 M biphenyl in the presence of (A) 0.5 mM 1a and (B) 0.6 mM 1c in benzene.

the substrates. However, that it was quenched by the substrates could be inferred from the observation that pulse-radiolytic ${}^3\text{MN}^*$, monitored at 425 nm, was efficiently quenched by them at the same concentrations. Note that MN has a lower E_T (60 kcal mol $^{-1}$) than biphenyl ($E_T = 66$ kcal mol $^{-1}$). It was necessary to perform sensitization experiments using ${}^3\text{BP}^*$ and ${}^3\text{MN}^*$ because we were apprehensive that ${}^3\text{CQ}^*$ might be quenched by the ene-hydrazine diones, at least in part, by an electron transfer mechanism with the latter acting as electron-rich donors.

It was important to see if stable products, with absorption spectra red shifted relative to those of the reactants, were formed under photoexcitation. We carried out steady state photolysis (366 nm) of 1a in benzene and methanol (both deaerated and air saturated) and noted the resultant absorption spectral changes. As shown in Fig. 4, while there is photochemical loss of absorbance in the region of ground state absorption of 1a, additional absorption indeed develops at 410 - 480 nm. O $_2$ (about 2 mM) is not found to have any effect on photoreaction yields. In benzene, in the absence of oxygen, the spectrum of the photolyzed solution remains unchanged over prolonged periods (observed over 2 - 4 days). However, in air-saturated benzene solution, the red-shifted absorption due to photoproduct(s) is slowly

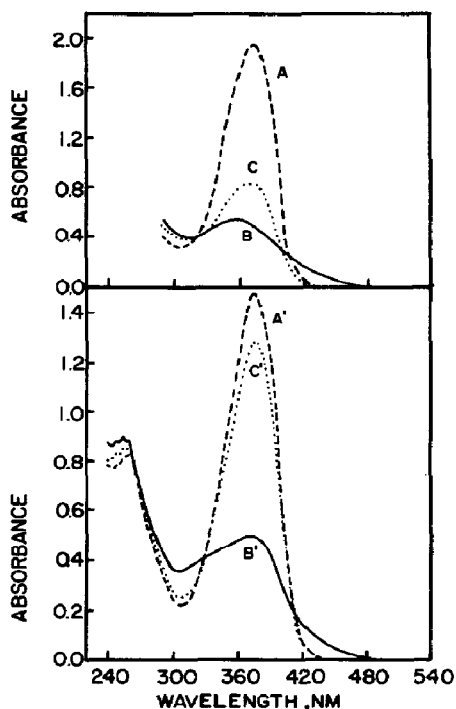


Fig. 4. Absorption spectral changes as a result of steady state photolysis (366 nm) of 1a in benzene (curves A - C) and in methanol (curves A' - C'). A and A', before irradiation; B, benzene solution after irradiation for 40 min; C, photolyzed solution in benzene (air saturated) after storage in the dark for 48 h; B', degassed methanol solution after irradiation for 70 min; C', photolyzed methanol solution (degassed) after storage in the dark for 72 h.

lost (over days) while the absorption in the region of the ground state spectrum (320 - 420 nm) is partially regained. In methanol, deaerated or air saturated, the ground state absorption is slowly regained at the expense of the photoinduced red-shifted absorption. All these results suggest that a "stable" product is photogenerated from **1a**, contributes to absorptions at long wavelengths (420 - 480 nm) and slowly reverts to the reactant in a protic solvent or in the presence of oxygen. Steady state spectral changes similar to those under direct excitation are also noted under 485 nm irradiation of CQ in the presence of 2.0 mM **1a** in benzene.

The most probable species responsible for the red-shifted absorption resulting from steady state photolysis is either the zwitterion **2** (Scheme I) or the trans isomer of the dibenzoylalkene. It is highly unlikely that a syn \rightleftharpoons anti hydrazone isomerization would cause a large red shift in the absorption spectrum of the *cis*-dibenzoylalkene chromophore (also see next paragraph). The pyrazoline **3** and the pyrazole **4** are easily ruled out on the basis that their absorption spectra are blue shifted relative to the parent substrates. This is actually observed for the isolated pyrazoles ($\lambda_{\text{max}} \approx 250$ nm for **4** in methanol) and is anticipated for pyrazolines because of the loss of interaction between the arylidene and benzoylalkene chromophores. We prefer an assignment in terms of the trans isomer rather than the zwitterion **2**, because the latter is unlikely to be stable (over days) and there is also no specific reason for it to revert to the reactants upon interaction with oxygen or a protic solvent. However, the trans isomer would slowly isomerize to the more stable *cis* form and this thermal isomerization would be catalyzed by charge transfer complexation with O₂ or protonation in a protic solvent. In spite of our best efforts, no trans isomers of the substrates could be isolated by usual work-up of the photolyzates following partial or exhaustive photolysis in benzene.

That the *cis*-*trans* isomerization about the alkene bond occurs in the course of the photolysis was conclusively established by an ¹H NMR analysis of the photolyzate from **1a** in C₆D₆ ($\lambda_{\text{ex}} = 366$ nm). Between photolysis and NMR measurement and during the transfer of the photolyzates to the NMR tubes, exposure of the solutions to oxygen was carefully avoided. It was found that, at the expense of the vinylic proton peak at $\delta = 6.20$ in the starting *cis* isomer (**1a**), a new peak developed in a slightly downfield region at $\delta = 6.36$ as a result of photolysis (Fig. 5). The latter is assigned to the vinylic proton in the *trans*-dibenzoylalkene isomer. The relative vinyl proton chemical shifts in *E* (*cis*) and *Z* (*trans*) isomers are well documented in the literature regarding enamine maleates/fumarates (formed from the reaction of secondary amines with dimethyl acetylenedicarboxylate) [31] as well as dibenzoylalkenes containing heterocyclic substituents [11, 32].

We interpret the absorption spectral change seen upon direct laser excitation as well as under triplet sensitization in terms of at least two photoproducts with closely overlapping spectra at 410 - 480 nm. One is a long-lived transient with its lifetime in the microsecond to millisecond domain; in view of the predominant photoreaction established by preparative photochemistry

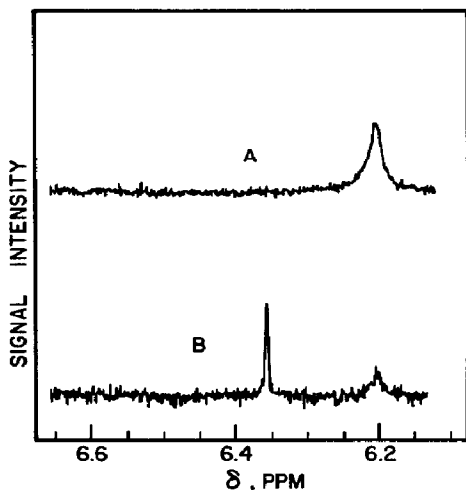


Fig. 5. ^1H NMR spectra (vinyl region) of (A) 1a and (B) the photolyzate from 1a, in C_6D_6 . The photolysis was carried out at 366 nm on 1 ml of about 5 mM 1a under argon saturation in a quartz cell of path length 2 mm (45 min, Bausch and Lomb SP-200 mercury lamp).

and product analysis, *i.e.* photocyclization (Scheme I), this species appears to be the zwitterion 2. The other photoproduct is permanent and is most probably the *trans* isomer of the dibenzoylalkene (as suggested by absorption spectral changes from steady state photolysis). The triplets of the dibenzoylalkene derivatives are very short lived (less than 50 ns), but this is not surprising in the light of possible intramolecular charge transfer, twisting about the alkene double bond and the photocyclization pathway. Our results show that the triplets are photoreactive. However, since they are short lived and elusive, their intermediacy under the condition of direct excitation could not be definitively established.

In summary, this time-resolved study has shown the photolytic formation of long-lived transients that are best described as zwitterionic intermediates in the course of intramolecular photocyclization of (*E*)-1-(2'-arylidene-1'-phenylhydrazinyl)-1,2-dibenzoylalkenes. In addition, there is evidence for geometric photoisomerization about the alkene double bond leading to *trans* isomers. Both of these phototransformations occur under direct excitation as well as under triplet sensitization. The triplets of the dibenzoylalkene substrates are short lived ($\tau \leq 50$ ns); both these and the triplet excited states of the zwitterions remain undetected on the nanosecond time scale.

Acknowledgments

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