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Intramolecular Photocyclization of 2-Vinylbiphenyl-Like Compounds. 2. Detection of the Intermediates and Kinetic Study by Laser Flash Photolysis of 1-(*o*-Diphenyl)-1-phenylethylene

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Abstract: Static fluorescence measurements and laser flash photolysis experiments have permitted the elucidation of the mechanism of photocyclization of 1-(*o*-diphenyl)-1-phenylethylene (a 1,1-diarylethylene). By fluorescence measurements, the quantum yield and the lifetime of fluorescence are found to be $\phi_f = 0.09$ and $\tau_f = 4 \times 10^{-9} \text{ s}^{-1}$, respectively. By flash photolysis, two transients species having different lifetimes have been observed. One, whose absorption has a maximum at 370 nm ($\epsilon_{\text{max}} (1.7 \pm 0.3) \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$), with a decay time on the order of 1 μs , is scavenged by oxygen ($k_Q = 1.0 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$). It has been assigned to the triplet state. The second one, absorbing in the visible ($\lambda_{\text{max}} 510 \text{ nm}$, $\epsilon_{\text{max}} (1.2 \pm 0.2) \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$) and below 300 nm, has a lifetime of the order of 1 ms. It is scavenged by oxidizing agents such as iodine ($k_I = 4.5 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$) and is attributed to a cyclic intermediate. By both continuous irradiation and flash photolysis, we find that the cyclic intermediate is formed from the singlet and triplet excited states, in the ratio 4:1. Rate constants as well as conversion yields of the main elementary reactions have been determined.

I. Introduction

The oxidizing photocyclization of hexatrienes having one or more double bonds engaged in an aromatic system has been extensively studied.²

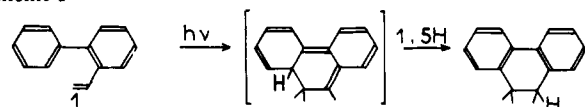
In the case where two consecutive double bonds are part of phenyl rings such as in **1**, the UV irradiation in a nonoxidizing media leads to a stable cyclic product which would be formed by a light-induced cyclization of the disguised hexatriene system, followed by a thermally allowed suprafacial 1,5 hydrogen shift.^{3–5}

The intermediate species postulated in this mechanism has never been observed.

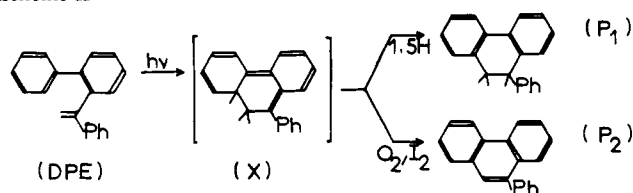
We report here evidence for this intermediate obtained by a laser flash photolysis study of the photocyclization of a 1,1-diarylethylene. A kinetic scheme is presented which accounts for the rates and products of the photoreaction.

We have chosen to study 1-(*o*-diphenyl)-1-phenylethylene (DPE), which gives under UV irradiation 9-phenyl-9,10-dihydrophenanthrene (P₁) in nonoxidizing media, while 9-phenylphenanthrene (P₂) is formed in the presence of oxidizing agents.

Scheme I



Scheme II



II. Experimental Section

1. Materials. The preparation of 1-(*o*-diphenyl)-1-phenylethylene has been described elsewhere.²

2. Fluorescence Measurements. Fluorescence decay curves were measured using the time-correlated single photon counting technique (PRA system).⁶ Fluorescence spectra and quantum yield of corrected fluorescence were measured with a spectrofluorimeter (Perkin-Elmer MPF.3). The solutions were unstable against prolonged exposure to the arc of the spectrofluorimeter; this effect was minimized by using very narrow slits and high gain.

3. Transient Absorption Measurements. The transient absorption measurements were made by laser photolysis using the fourth harmonic at 265 nm of a Q-switched neodymium laser (Quantel instrument) delivering approximately 80 mJ of radiation in 3 ns. The analyzing beam from a pulsed 75-W xenon lamp was perpendicular to the laser beam and passed through a quartz cell (10 mm square, all four sides polished) containing the sample. The apparatus and the techniques have been described elsewhere.⁷

Table I. Comparison of Some Spectral Properties of Diphenyl- and 1-(*o*-Diphenyl)-1-phenylethylene in Cyclohexane as Solvent

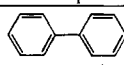
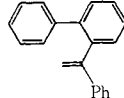
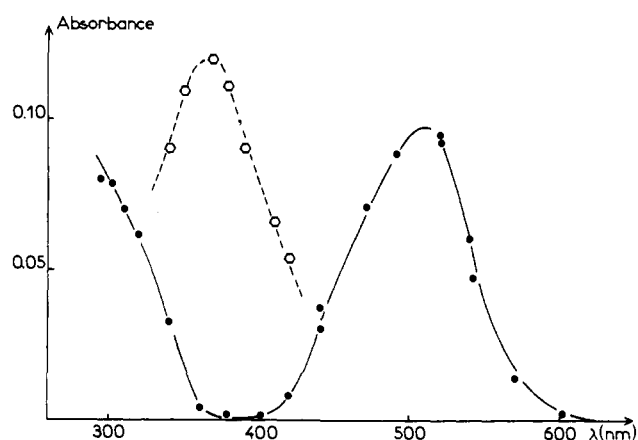
compd	absorption		emission		decay time τ , ns
	λ_{\max} , nm	ϵ , $10^4 \text{ M}^{-1} \text{ cm}^{-1}$	λ_{\max} , nm	ϕ_F	
	247	1.5	305 318	0.18	16.0
	245	2.8	310 322	0.09	4.0

Table II. Oxygen Effect on the Lifetime of the Transient Species Absorbing at 510 and 370 nm

solution	$[\text{O}_2]$, M	absorption at 510 nm		absorption at 370 nm	
		τ , ms	$1/\tau = \Sigma k + k_Q[\text{O}_2]$, s^{-1}	τ	$1/\tau = \Sigma k + k_Q[\text{O}_2]$, $\times 10^{-5} \text{ s}^{-1}$
degassed		6.1	164	1.75 μs	5.7
aerated	$\sim 2.3 \times 10^{-3}$	4.40	225	400 ns	25
O_2 -saturated	$\sim 1.1 \times 10^{-2}$	2.40	417	87 ns	115

**Figure 1.** Absorption spectra observed by laser flash photolysis of DPE. Dotted line: triplet absorption. Full line: cyclic intermediate.

III. Results

Quantum Yield and Lifetime of Fluorescence. The absorption and fluorescence spectra of DPE in cyclohexane solutions are quite similar to those recorded for biphenyl in the same solvent⁸ (see Table I) except for a red shift of the fluorescence spectra. The quantum yield of fluorescence ϕ_f of DPE was determined by comparison of its intensity of fluorescence with the case of biphenyl for which ϕ_f is known ($\phi_f = 0.18$) under the same experimental condition. It was found to be $\phi_f = 0.09$.

The lifetime of fluorescence of DPE in degassed solution ($3 \times 10^{-5} \text{ M}$ in cyclohexane) obtained by the single photon counting technique was determined using 306-nm excitation while monitoring emission at 325 nm. Using an iterative convolution by a least-squares method,⁶ a single exponential fluorescence decay was obtained, giving a lifetime of 4.0 ns at 25 °C.

Transient Absorption Measurements. By laser flash photolysis of DPE in degassed cyclohexane solutions, two transient absorptions, distinguishable by their decay time, were observed between 290 and 600 nm.

(1) The first intermediate, having a "long decay time" in the millisecond range, appeared in the red (λ_{\max} 510 nm) and in the UV ($\lambda_{\max} < 300 \text{ nm}$). The species that gives rise to this absorption disappears by a first-order process with a rate constant of $1.60 \times 10^2 \text{ s}^{-1}$. Measurements at wavelengths shorter than 300 nm are difficult and rather inaccurate since

the fluorescence emission and the permanent absorption due to the photoproduct interfere with one another.

(2) The second intermediate, having a decay time in the microsecond range, appeared between 340 and 440 nm with a maximum at 370 nm. This transient absorption also disappears by a first-order process with a rate constant of $5.75 \times 10^5 \text{ s}^{-1}$ in degassed solutions (see Figure 1).

To identify the nature of these transient species and their role in the kinetics of the reaction scheme, further experiments were performed.

Oxygen Effect. By photolysis in continuous illumination,² it was shown that the UV irradiation of DPE leads to a cyclic nonoxidative product, 9-phenyl-9,10-dihydrophenanthrene (P_1), either in degassed or aerated cyclohexane solution. The total quantum yield was found to be slightly but significantly different when the measurements were carried out in both the presence and absence of oxygen. The values obtained were 0.20 and 0.24, respectively. In laser photolysis experiments, the product P_1 can be detected by its stable absorption in the UV spectral region.

We looked for an effect of oxygen in the decay kinetics of the transient absorptions in degassed, aerated, and O_2 -saturated solutions. It was found that oxygen has a small influence on the decay of the species having "a long lifetime" but is a very efficient scavenger of the short lifetime transient species (see Table II). From the plot of the reciprocal measured lifetimes as a function of O_2 concentration ($1/\tau = 1/\tau_0 + k_Q[\text{O}_2]$) the value of the rate constant for oxygen quenching, k_Q , was found to be equal to 2.3×10^4 and $1.0 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$, respectively, for the long- and short-lived transient species.

From examination of the effects of oxygen on the formation of the transient absorption, the following observations can be made.

(1) The transient absorption at 370 nm is formed during the laser pulse duration (3 ns) whatever the O_2 concentration.

(2) In either O_2 -saturated or aerated solution, the species absorbing at 510 nm is also produced during the laser pulse; in the degassed solution the optical density still increases slowly during the dark period following the irradiation. This can be seen in Figure 2 where OD at 510 nm is plotted as a function of the time. It can be seen that the contribution of the slowly growing transient absorption is approximately 20% of the entire transient absorption.

Plotting $\ln(\text{OD}_{\max} - \text{OD}_t)$ as a function of time, we found that this slow process of formation follows first-order kinetics with a rate constant $k = 5 \times 10^5 \text{ s}^{-1}$ which is quite close to the

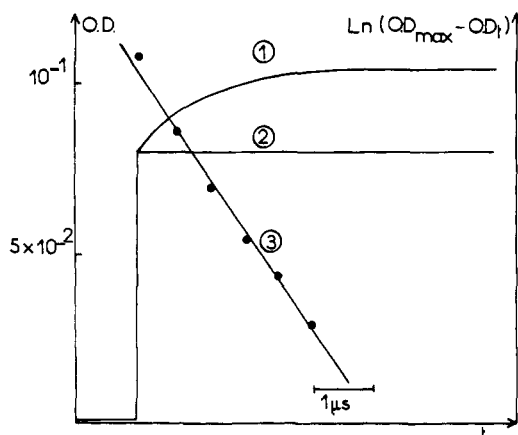


Figure 2. Transient optical density at 510 nm vs. time: (1) in degassed solutions; (2) in aerated or O₂-saturated solutions; (3) ln(OD_{max} - OD_t) vs. time.

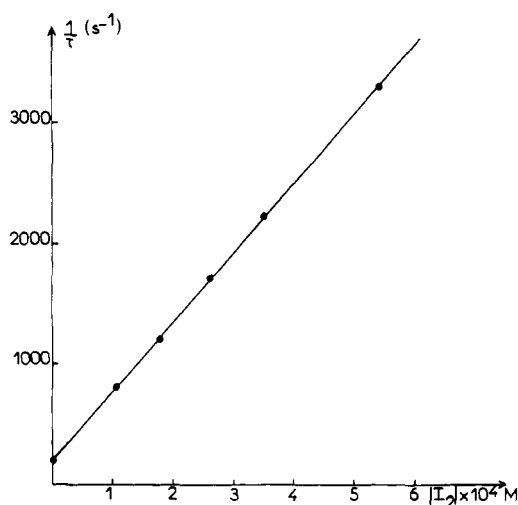


Figure 3. Reciprocal lifetime of the transient absorption at 510 nm as a function of the concentration of I₂.

value found for the decay of the transient absorption band at 370 nm.

Iodine Effect. In the preceding paper it was shown that in the presence of iodine, the continuous irradiation of DPE leads to an oxidizing cyclization giving the product P₂ as a new final product at the expense of the nonoxidizing process giving P₁.

In laser flash photolysis experiments, when the iodine concentration is gradually increased up to 5.5×10^{-4} M, the decay time of the short-lived transient (370 nm) is not significantly changed while that of the long-lived transient (315, 510 nm) decreases strongly. From the slope of the straight lines obtained by plotting the reciprocal decay time at 510 and 315 nm as a function of I₂ concentration (Figure 3) the rate constant of the reaction of iodine with the long-lived transient is found to be $k_{12} = 4.5 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$.

As the iodine concentration increases a residual permanent absorption appears at 315 nm after the decay of the transient absorption related to the long-lived species. This permanent absorption is due to the 9-phenylphenanthrene, P₂, the extinction coefficient of which is around 1800 at 315 nm.⁹ This allows evaluation of the amount of P₂ formed in a single laser pulse for a given I₂ concentration. This amount of P₂ increases as the I₂ concentration increases but tends to a limitative value for $[I_2] > 5 \times 10^{-4}$ M. The ordinate intercept of the straight line obtained by plotting $1/[P_2]$ vs. $1/[I_2]$ gives the maximum

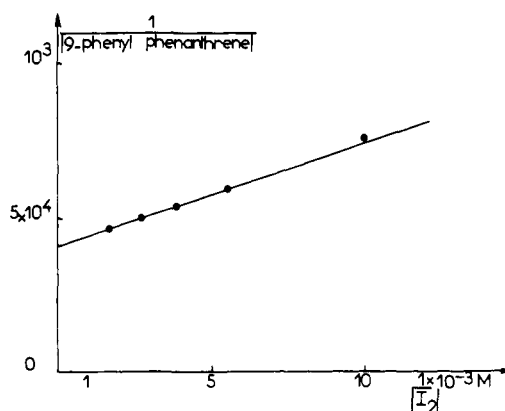


Figure 4. Reciprocal maximum concentration of 9-phenylphenanthrene against the reciprocal concentration of I₂.

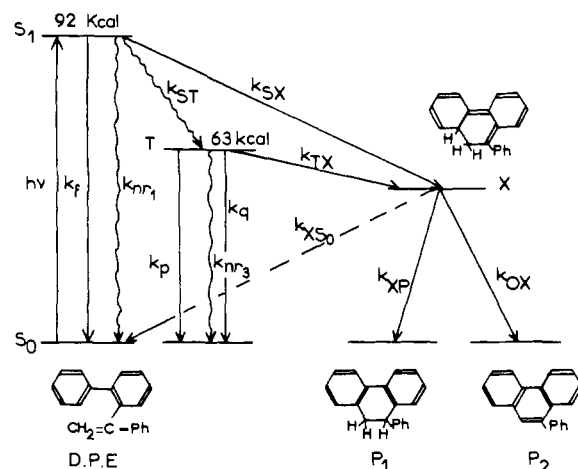


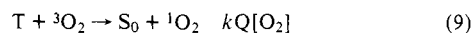
Figure 5. Schematic diagram of the oxidizing and nonoxidizing photocyclization of 1-(*o*-diphenyl)-1-phenylethylene.

concentration of P₂ which could be found, $[P_2]_{\text{max}} = (2.2 \pm 0.4) \times 10^{-5}$ M (see Figure 4).

III. Interpretation

The experimental data described above can be given a consistent interpretation, assuming the mechanism of Scheme III (see Figure 5).

Scheme III



In this mechanism, one must note that the cyclic intermediate product X could be formed in steps 5 and 6, via the singlet and triplet pathways. It has also been considered that the species X can give back the ground state by reversible opening (step 11) as has been shown to be the case for the similar molecule, 1,2-diarylethylene.²⁻⁴

Assignment of the Transient Absorptions. The decrease of the lifetime of the transient species absorbing at λ_{\max} 370 nm, as the O₂ concentration is increased, suggests that this species should be assigned to the triplet state. The unusually short lifetime ($\sim 1.7 \mu\text{s}$) in degassed medium is not surprising if one considers that the triplet state contributes to the photocyclization, via the intermediate X.

The species having a long lifetime, with a maximum of absorption at 510 nm and below 300 nm, is attributed to the intermediate X. This is produced by an intramolecular cyclization from both the singlet and triplet state, since it is formed both during the laser pulse duration and in the dark period following excitation.

The mechanism of formation of X is confirmed if one considers the following.

(1) The lifetime of the singlet state is 16 ns in the case of biphenyl while it is only of the order of 4 ns in the case of DPE, implying the existence of an extra deactivation pathway; this additional deactivation process can be attributed to the cyclization process.

(2) The decay of the triplet state and the slow formation of X have approximately the same rate constant.

Evaluation of the Extinction Coefficient of the Transient Bands. In order to evaluate the extinction coefficient of a transient species in a flash photolysis experiment one must know the absorbance of the transient and the concentration of the species. The concentration of X formed by a single laser pulse can be deduced from that of the final products P₁ and P₂ whose ratio depends on the experimental conditions, if it is assumed that the conversion of X in P₁ or P₂ is quantitative; the concentration of the stable products P₁ and P₂ can be measured by straightforward colorimetry.

However, if a reversible opening of X (reaction 1) occurs, the concentration of X could be underestimated.

Combined experiments by continuous irradiation and laser flash photolysis show that the reaction 11 is inefficient compared to reactions 10 + 12. Indeed, in continuous irradiation the quantum yields of product formation in degassed or in aerated solutions containing iodine at 5×10^{-4} M are almost identical: $\phi_{P_1} = 0.24$ and $\phi_{P_1+P_2} = 0.04 + 0.22 = 0.26$. From laser photolysis measurements it was found that addition of this amount of iodine decreases the lifetime of X by a factor of 20. The yield of X \rightarrow S₀ should be similarly reduced. If the slight increase in quantum yield noted above were significant, it could be due to a reversible opening. The effect, however, must be small, since on the basis of these data, the yield of conversion of X to products is at least 0.92.

By measuring [P₁] or [P₂] by the change of the optical density at 300 or 315 nm, respectively, the extinction coefficient of X has been deduced to be $\epsilon_{510\text{nm}} = (1.1 \pm 0.2) \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$. The extinction coefficient of the triplet species at 370 nm is evaluated as follows.

From laser photolysis measurements, we found that about 20% of the X species is produced through the triplet pathway. Thus the concentration of triplet produced by a single laser pulse is given by $0.2[X] \approx \phi_{TP_1}[T]$ and with $[X] = (2.2 \pm 0.4) \times 10^{-5} \text{ M}$, $[T] = (7.6 \pm 1.5) \times 10^{-6} \text{ M}$ leading to an extinction coefficient value $\epsilon_{370\text{nm}}$ of $(1.7 \pm 0.3) \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$. The limited accuracy of the $\epsilon_{510\text{nm}}$ and $\epsilon_{370\text{nm}}$ values is related to the difficulty of knowing P₁ and P₂ concentrations. The accuracy of the ϵ_{300} (P₁) and ϵ_{315} (P₂) are similarly limited, since the wavelengths 300 and 315 nm are on the steeply rising side of the absorption bands of P₁ and P₂.

Table III. Values of the Lifetimes, Rate Constants, and Yields Measured or Deduced in the Photocyclization of DPE

$\tau_f = 4. \text{ ns}$	$k_f = 2.25 \times 10^7 \text{ s}^{-1}$
$\tau_T = 1.75 \mu\text{s}$	$k_p < 1 \text{ s}^{-1}$ at 77 K
$\tau_X = 6.1 \text{ ms}$	$\phi_{P_1} = 0.24$
$k_{SX} = 5.2 \times 10^7 \text{ s}^{-1}$	$\phi_{P_2} = 0.22$
$k_{ST} = 1.3 \times 10^7 \text{ s}^{-1}$	$\phi_f = 0.09$
$k_{TX} = 3.3 \times 10^5 \text{ s}^{-1}$	$\phi_{SX} = 0.21$
$k_{XP_1} = 1.6 \times 10^2 \text{ s}^{-1}$	$\phi_{ST} = 0.05$
$k_{I_2} = 4.5 \times 10^6 \text{ s}^{-1}$	$\phi_{TX} = 0.58$
$k_{nr1} = 1.6 \times 10^8 \text{ s}^{-1}$	$\phi_{XP} = 1$
$k_{nr3} = 2.4 \times 10^5 \text{ s}^{-1}$	

Evaluation of the Rate Constants and of the Internal Conversion Yield. Data obtained by fluorescence, flash photolysis, and continuous irradiation measurements are summarized below.

$$\tau_f = 1/(k_f + k_{nr1} + k_{ST} + k_{SX}) = 4 \times 10^{-9} \text{ s} \quad (\text{I})$$

$$\phi_f = \tau_f k_f = 9 \times 10^{-2} \quad (\text{II})$$

$$\tau_T = 1/(k_{TX} + k_p + k_{nr3}) = 1.75 \times 10^{-6} \text{ s} \quad (\text{III})$$

$$\tau_X = 1/(k_{XP} + k_{XS_0}) = 6.1 \times 10^{-3} \text{ s} \quad (\text{IV})$$

$$\phi_{TP} = \phi_{TX} \phi_{XP_1} = 0.58 \quad (\text{V})$$

$$\phi'_{SP_1} = \phi_{SX} \phi_{XP_1} + \phi_{ST} \phi_{TX} \phi_{XP_1} = 0.24 \quad (\text{VI})$$

$$\phi_{SP_1} = \phi_{SX} \phi_{XP_1} = 0.21 \quad (\text{VII})$$

when the triplet state is quenched by piperylene

From this set of results, the following rate constant can be deduced:

$$k_f = \phi_f / \tau_f = 2.25 \times 10^7 \text{ s}^{-1}$$

Since the phosphorescence lifetime is a few seconds at 77 K² the rate constant of phosphorescence emission k_p is smaller than 1 s^{-1} and can be neglected in comparison with other processes occurring at room temperature. From the triplet lifetimes measured in flash photolysis we found that $k_{TX} + k_{nr3} = 5.7 \times 10^5 \text{ s}^{-1}$. Since ϕ_{XP_1} is equal to or very near unity ($\phi_{XP_1} > 0.92$) we have directly $k_{XP_1} = 1.64 \times 10^2 \text{ s}^{-1}$ and from eq V, $\phi_{TX} = 0.58 = k_{TX} \tau_f$ and thus $k_{TX} = 3.3 \times 10^5 \text{ s}^{-1}$; from eq VII, $\phi_{SX} = k_{SX} \tau_f \approx 0.21$ and thus $k_{SX} = 5.2 \times 10^7 \text{ s}^{-1}$; from eq VI and VII $\phi_{ST} \phi_{TX} = 0.03$ and with $\phi_{TX} = 0.58$, we obtain $\phi_{ST} = 0.05 = k_{ST} \tau_f$ ($k_{ST} = 1.3 \times 10^7 \text{ s}^{-1}$); from eq III giving $k_{TX} + k_{nr3}$ and from eq V giving k_{TX} , we have $k_{nr3} = 2.4 \times 10^5 \text{ s}^{-1}$; from eq I and the calculated values of k_f , k_{ST} , k_{SX} , we have $k_{nr1} = 1.6 \times 10^8 \text{ s}^{-1}$.

It is important to note that, although the number of parameters involved in the proposed mechanism is large, many different methods of measurements have been used to separate the rate processes involved. The accuracy of the rate constants and of the quantum yields of conversion *deduced* from primary data have errors which we estimate to be $\pm 10\%$. The accuracy of rate constants calculated from *differences* between experimental measurements is more limited, as, for instance, is the case for the value of k_{ST} which arises from a small difference between ϕ' and ϕ (eq VI and VII). Taking into account an accuracy of 5% on ϕ' and ϕ , we estimate $0.01 < \phi_{ST} \phi_{TX} < 0.06$ and thus $4.3 \times 10^6 \text{ s}^{-1} < k_{ST} < 2.6 \times 10^7 \text{ s}^{-1}$. A more precise value of k_{ST} can be obtained from flash photolysis measurements, since 20% of X is formed via the triplet pathway. That implies that $\phi_{SX} \approx 4 \phi_{ST} \phi_{TX}$ and with the values of ϕ_{SX} (0.21) and ϕ_{TX} (0.58) this gives $\phi_{ST} \sim 0.1$ and thus $k_{ST} = 2.5 \times 10^7 \text{ s}^{-1}$. All the measured and calculated results are collected in Table III.

IV. Conclusion

A kinetic scheme for the photocyclization of 1-(*o*-diphe-

nyl)-1-phenylethylene is proposed based on product analysis, fluorescence measurements, and transient species detected by flash photolysis experiments.

The rate of photocyclization from the singlet state is 100 times faster than the apparent cyclization rate constant from the triplet state. This can be accounted for in the following manner.

(1) The intermediate X, being a ground-state singlet species, can be formed more easily from an excited state of the same multiplicity and probably via an electrocyclic ring-closure route.

(2) The energetic factors can be important. If one assumes the existence of a common transition state from the excited singlet and triplet states to produce X, it would follow that the activation energy would be smaller for reaction from the singlet state than from the triplet state. Hence photocyclization from the singlet state would be favored kinetically.

(3) It is more likely, according to the results described in part 1,² that the mechanisms of formation of X via the singlet and triplet state would be different, since the twisting of the double bond will differ in these two states affecting the spatial arrangement of the atoms to be linked.¹⁰

Further experiments will be carried out with other diarylethylenes.

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References and Notes

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- (9) At this wavelength, which is on the steeply rising side of the absorption band of P₂, the slits of the monochromator are around 0.5 mm, giving a resolution of 3 mm. It follows that $\epsilon_{315nm} = 1800 \pm 350 \text{ M}^{-1} \text{ cm}^{-1}$.
- (10) The values of the rate constants k_{TX} and k_{Tn3} have been evaluated by assuming that the triplet state observed by flash spectroscopy is the cyclizing species. On account of its lifetime, this triplet should be a "planar" state, the ethylenic CH₂ still being in the molecular plane. On the contrary, if the cyclization of the triplet occurs after rotation of the double bond, on one hand, the lifetime of the observed triplet would give the rate of rotation of the double bond and not that of cyclization; on the other hand, the rate of cyclization of the "twisted" triplet should be much larger than the $3.3 \times 10^5 \text{ s}$ value reported above, since its lifetime must be much shorter than 1.75 μs .

π, π -Biradicaloid Hydrocarbons. The Pleiadene Family. 4.¹ Involvement of Upper and/or Hot Excited Singlet and Triplet States in a Photochemical Conversion of a Polycyclic Cyclobutene to a Butadiene

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Abstract: The mechanism of the photochemical electrocyclic transformation of the cyclobutene **2** to pleiadene **1** in a rigid glass (77 K) with long-wavelength light involves successive absorption of two photons, with triplet **2** as the intermediate state. At shorter wavelengths, the reaction proceeds by the ordinary one-photon mechanism. It is concluded that thermalized S₁ and T₁ states are unreactive and that the reaction occurs in upper and/or hot excited states with quantum yields of the order of 1%. It is pointed out that the common practice of ignoring such possible upper and/or hot excited state contributions to unimolecular photochemical reactivity of organic molecules in solution is questionable.

The photochemical preparation of pleiadene (**1**) by irradiation of the cyclobutene precursor **2** in rigid organic glasses has been reported.^{3,4} Alkyl derivatives^{5,6} as well as more highly condensed polycyclic analogues^{4,7} are similarly accessible. We now wish to report in detail our mechanistic investigation of this photochemical cyclobutene \rightarrow butadiene conversion. Its unusual nature has already been briefly described^{4,7-9} and the theoretical implications were discussed.¹⁰⁻¹²

Results

Excited States of 1 and 2. The absorption spectrum of **1** and seven of its alkyl derivatives was reported and analyzed previously.^{5,6} The energies, polarizations, and relative intensities of the first six transitions were in excellent agreement with π -electron calculations, which led to an assignment of the second excited singlet state as doubly excited. The first tran-

sition is short-axis polarized and lies in the near-IR region (0-0 band at 11 700 cm^{-1}); no fluorescence was observed. The lowest triplet is calculated to lie only about 3000 cm^{-1} above the singlet ground state and no experimental evidence for it has been obtained. In a rigid glass at 77 K, **1** is stable for many hours, both in the dark and under UV irradiation.

The absorption and uncorrected fluorescence and phosphorescence spectra of **2** are shown in Figure 1 and correspond well to expectations for noninteracting acenaphthene and benzocyclobutene chromophores. The absorption reveals the expected presence of the three low-energy transitions of the naphthalene chromophore (N1 = ¹L_b, N2 = ¹L_a, N3 = ¹B_b) and of the lowest benzene transition (B1 = ¹L_b). Polarization measurements on these transitions¹³ by the stretched polymer method are in perfect agreement with expectations, given the C_s symmetry and the 115° dihedral angle between the plane