Intramolecular Photocyclization of 2-Vinylbiphenyl-Like Compounds. 1. A Quantitative Study of the Cyclization under Steady-State Illumination

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Abstract: The quantum yield of cyclization, from S_1 and T_1, of 1-(o-diphenyl)-1-phenylethylene (Ia) and 1-(4-fluorenyl)-1-phenylethylene (Ib) has been measured. From the mechanism established in the following paper and the lifetimes of the reactive states for these molecules, we have deduced their relative reactivity. As expected for an electrocyclic reaction the singlet cyclizes faster than the triplet. The efficiency of the reaction from the singlet state for arylethylene is enhanced as the molecular geometry approaches planarity. The failure of the triplet of Ib to undergo cyclization, in contrast to the efficient cyclization of the triplet of Ia, points to a different geometric requirement in that case and therefore to a different mechanism of cyclization for Ia–c which depends upon the multiplicity of the photoreactive state. A fast intramolecular hydrogen transfer, which corresponds to a relatively oxidant insensitive reaction, needs a flexible intermediate, but the efficiency of the product formation is not related to the rate of the hydrogen transfer since in the absence of oxidant the path taken is the only possible one for the irreversibly formed intermediate X.

The oxidative photocyclization of hexatrienes where one or several double bonds have been incorporated into an aromatic system appears to be of great value in the synthesis of polynuclear hydrocarbons. 1,2-Diarylethylenes have been investigated from a synthetic and mechanistic point of view.[2] On the other hand, similar reactions with 1,1-diarylethylenes have received relatively little attention. We[3] and Padwa[4] have observed some nonoxidative photocyclizations which form six-membered rings and we have discovered a five-membered carbocyclic ring formation by an amine-catalyzed photocyclization of 1,1-diarylethylenes.[5]
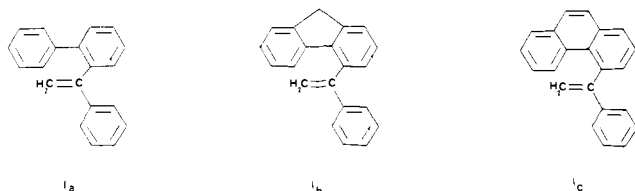
We wish now to describe a comparative study of the photocyclization of three 1,1-diarylethylenes which possess a disguised hexatriene system and which can form a stable photoproduct by rearrangement of the primary product of the cyclization.

Laarhoven,[6] Horgan,[7] and Padwa[4] have proposed that the photocyclization of structurally similar compounds occurs in two steps; a light-induced cyclization of the hexatriene system followed by a thermally allowed suprafacial 1,5-hydrogen shift.[8]
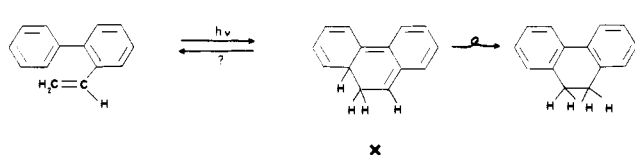
But the intermediate (X) has never been detected and the possibility of its reversal formation had to be tested since that could be the limiting factor in the synthesis of polynuclear hydrocarbons by the photocyclizations of arylethylenes. A relevant and intriguing observation was the increased sensitivity to oxygen of the photocyclization, from 2-vinylbiphenyl to 4-vinylphenanthrene.[7]

In this paper and its companion we have identified the photoproducts formed by irradiation of Ia–c with and without the presence of oxidant, measured the efficiency and the apparent reactivity of the singlet and triplet excited states of Ia,b for cyclization (part 1), and established by a flash photolysis study the mechanism assumed by previous authors (part 2).

Results

Substrates. Addition of PhLi to 2-biphenylcarboxylic acid gives 2-benzoylbiphenyl;[9] a treatment with MeMgI and dehydration yields Ia.[10] We have prepared Ib for the first time from reaction of 4-benzoylfluorene[11] with MeMgI followed by a dehydration.

The Friedel–Crafts (FC) acylation of phenanthrene does not involve substitution at the 4 position[12] so a complete synthesis of Ic has been undertaken starting with a FC reaction between naphthalene and succinic anhydride.[13] The β isomer is reduced,[14] alkylated with ethyl oxalate, and cyclized to 4-(1',2'-dihydro)phenanthrylcarboxylic acid. After esterification, dehydrogenation, and hydrolysis 4-phenanthrylcarboxylic acid is obtained.[15] Treatment with $SOCl_2$ followed by addition of PhMgBr gives 4-benzoylphenanthrene which was not previously known but has been identified by its spectroscopic properties (IR, NMR). Addition of 4-benzoylphenanthrene with CH_2I_2 to an amalgam magnesium gives the previously unknown Ic.

Photoproducts. Irradiation of the degassed cyclohexane solutions of Ia–c (4×10^{-3} M), at 300 nm, leads exclusively to IIa–c.

IIa has been described previously;[16] IIb and IIc have been identified spectroscopically (Experimental Section) and by their dehydrogenation to IIIc which was known[17] and to IIIb which was identified by its spectroscopic and analytical data.

When cyclohexane solutions of Ia–c (4×10^{-3} M) and iodine (1.8×10^{-3} M) bubbled with oxygen were irradiated only

Scheme I

Scheme II

X

Scheme III

I a,b,c   II a,b,c   III a,b,c

a Z = 2H
b Z = CH_2
c Z = CH=CH
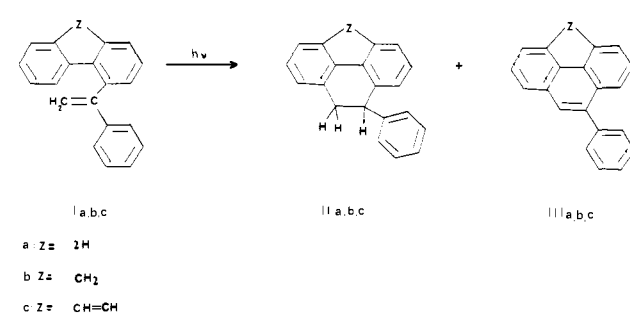
Table I. Quantum Yields of Photocyclization of Ia and Ib

compd	solvent	oxidant or quencher	ϕ_{II}[b]	ϕ_{III}[b]
Ia[a]	cyclohexane	N$_2$ saturated	0.24 ± 0.01	0.00
	cyclohexane	air saturated	0.23 ± 0.01	0.00
	cyclohexane	O$_2$ saturated	0.20 ± 0.01	0.00
	cyclohexane	1,3-pentadiene (4 × 10^{-3} M)	0.21 ± 0.01	0.00
	cyclohexane	air saturated + iodine (5$^-$ × 10^{-4} M)	0.04 ± 0.01	0.22 ± 0.02
Ib[a]	cyclohexane	degassed solution	0.33 ± 0.01	0.00
	cyclohexane	air saturated	0.02 ± 0.01	0.12 ± 0.01
	cyclohexane	oxygen saturated	0.00	0.12 ± 0.01
	cyclohexane	1,3-pentadiene (4 × 10^{-3} M)	0.33 ± 0.01	
	cyclohexane	degassed cyclohexane + iodine (10^{-4} M)	0.02 ± 0.01	0.33 ± 0.01

[a] Concentration 10^{-4} M, conversions ~5–10%. [b] The amounts of II and III were calculated from VPC and the ferrioxalate actinometry,[18] in the modification described by Demas,[19] was used to measure the light intensity.
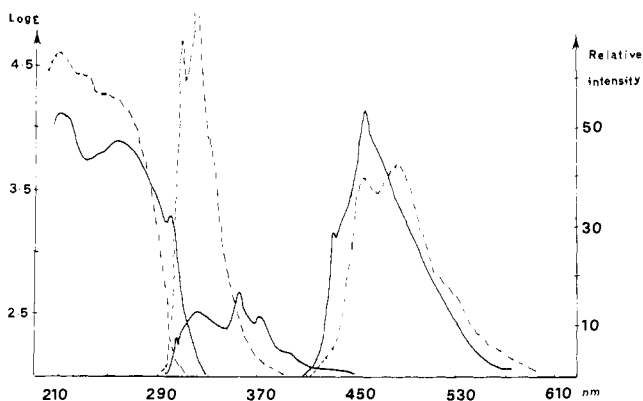
Figure 1. Absorption, fluorescence, and phosphorescence of Ia (- - - -) and Ib (—) excited at 280 nm.

oxidative photocyclization occurred and we obtained directly IIIa-c. If IIa-c are irradiated under the same conditions IIIa-c are not formed.

When the oxidant is only a stream of oxygen, Ia gives only IIa, Ib gives IIIb, and Ic → IIc (41%) + IIIc (59%). The irradiation of Ia with CDCl$_3$ as solvent does not incorporate deuterium in IIa.

Quantum Yields. Ia and Ib, whose behavior in the presence of oxygen represents extreme cases, have been studied in detail. Their quantum yields of photocyclization, at 253.7 nm, have been measured in degassed cyclohexane solution, in the presence of different oxidants (O$_2$, I$_2$) and with increasing amounts of *trans*-piperylene ($E_T \simeq 59$ kcal mol^{-1}) as triplet quencher (Table I).

By sensitization with benzophenone (2.2 × 10^{-2} M), using benzene as solvent, we measured $\phi_{IIa \text{ sens}}$ with increasing concentration of Ia. Under the stationary state approximation a linear correlation is expected between $1/\phi_{IIa \text{ sens}}$ and $1/[Ia]$, i.e.,

$$\frac{1}{\phi_{IIa \text{ sens}}} = \frac{1}{\phi_{TX}} + \frac{1}{\phi_{TX}k_t\tau_{Tsens}}\frac{1}{[Ia]}$$

where τ_{Tsens} is the lifetime of the triplet state of benzophenone in the absence of Ia, a quantity which has been measured by Singer[20] to have the value $\tau_{Tsens} = 6.9 \times 10^{-6}$ s, k_t is the energy transfer rate constant, and ϕ_{TX} is the quantum yield of reaction for the triplet state of Ia. Our data (Table II) gave a linear plot of $1/\phi_{IIa \text{ sens}}$ vs. $1/[Ia]$ with an intercept of 1.72 and a slope of 0.073 × 10^{-2} M from which we deduced that $\phi_{TX} = 0.58$ and $k_t = 3.4 \times 10^8$ s. Since the lifetime of T$_{sens}$ is very sensitive to the presence of impurities this value of k_t must be considered as only approximate.

In contrast to the case of Ia benzophenone does not sensitize the photocyclization of Ib. Even when a high triplet energy

Table II. Quantum Yield of Sensitized Formation of IIa,b

compd	concn	$\phi_{II \text{ sens}}$
Ia	4.5 × 10^{-4}	0.30
	9 × 10^{-4}	0.39
	1.35 × 10^{-3}	0.42
	2.25 × 10^{-3}	0.49
Ib	4.5 × 10^{-4}	0.00
	2.25 × 10^{-3}	0.00
	1.1 × 10^{-2}	0.00
	4.4 × 10^{-2}	0.00

sensitizer, such as acetone, is used as solvent, we observe the formation of only a very small amount of IIb which is not quenched in presence of 2 × 10^{-2} M of piperylene and therefore can be attributed to a singlet sensitization.

Lifetime and Energy of Excited States. The energies (kcal mol^{-1}) of S$_1$ and T$_1$ of Ia,b have been estimated from fluorescence and phosphorescence spectra (Figure 1): Ia, $E_{S_1} = 92$, $E_{T_1} = 63$; Ib, $E_{S_1} = 94$, $E_{T_1} = 66.7$.

The singlet states lifetimes of Ia,b have been measured in cyclohexane by the single photon technique:[21] Ia, $\tau_{S_1} = 4 \times 10^{-9}$ s at 3 × 10^{-5} M; Ib, $\tau_{S_1} = 2.5 \times 10^{-9}$ s at 10^{-3} M.

The triplet lifetime of Ia has been obtained by following the decay of the intensity of phosphorescence at 77 K: Ia, $\tau_{T_1} = 3.1$ s; Ib, $\tau_{T_1} = 0.92$ s.

By flash photolysis[21] the triplet lifetime is obtained at room temperature in degassed cyclohexane at the concentration (10^{-4} M) used for the determination of the quantum yield of photocyclization: $\tau_{T_1} = 1.75 \times 10^{-6}$ s for Ia.

Discussion

Mechanism. The same relative sensitivity to oxygen for the photocyclization of compounds Ia,c and of 2-vinylbiphenyl and 4-vinylphenanthrene[7] points to similar mechanisms of reaction in these cases. The increased sensitivity to oxygen of Ib with regard to Ic made it most suitable for comparison with the less sensitive Ia. The lack of effect of PhSe radicals and the absence of H$_2$O$_2$ when irradiations were conducted in presence of O$_2$ had led Horgan[7] to discard a radical chain mechanism. We have not observed incorporation of deuterium when Ia was irradiated in CDCl$_3$; moreover, the quantum yield of cyclization ($\phi_{II} + \phi_{III}$) remains almost constant with iodine present when the lifetime of the intermediate[21] is decreased by a factor of 20. These observations taken together are good evidence for an *irreversible cyclization followed by a competitive formation of II and III*. The first step would be a 6π-electrocyclic reaction, with the second step an allowed, suprafacial 1,5 hydrogen shift which would be in competition with abstraction of this hydrogen by O$_2$ or iodine.

The intermediate X has been detected for the first time and

Scheme IV
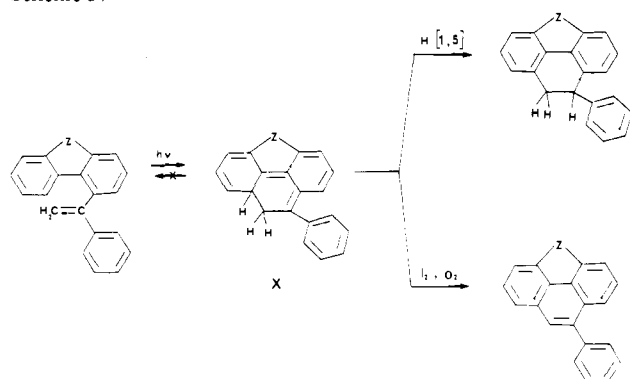
its evolution measured by flash photolysis; the detailed discussion of the evolution of the excited states of Ia and of X will be presented in the companion paper.[21] With the results reported here we have been able to identify the photoreactive states and measure their reactivity, the efficiency of their cyclization, and the effects of structural changes in the biphenyl part of the molecule on the reaction.

Multiplicity of the Reactive States and Efficiency of the Cyclization. The comparison of the quantum yield of cyclization, by direct irradiation with and without triplet quencher (piperylene), gives the quantum yields of cyclization from S_1 and T_1: Ia, $\phi_{SX} = 0.21$; $\phi_{ST}\phi_{TX} = 0.03$; Ib, $\phi_{SX} = 0.33$ and $\phi_{ST}\phi_{TX} \sim 0.00$.

The effect of oxygen is difficult to understand since it can quench the singlet state to produce the triplet state,[22] deactivate the triplet state, and interact with the intermediate (X). Since IIa,b are not oxidized by O_2 under the irradiation conditions, the products of the irradiation of Ia,b in the presence of O_2 indicate that the intermediate (Xa) coming from Ia transfers its hydrogen faster than it is oxidized in contrast to the case for Xb originating from Ib.

This different behavior is probably due to a slower hydrogen transfer from Xb, which is less flexible than Xa, making it more difficult to reach the 9,10-dihydrophenanthrene conformation.[23] This point of view is supported by the very different lifetime of the irreversibly formed Xa and Xb in the absence of oxidant[21] ($\tau_{Xa} = 6 \times 10^{-3}$ s, $\tau_{Xb} > 1$ s). In oxygen-saturated cyclohexane solution IIIa is not formed, although the lifetime of Xa is reduced by a factor of 3.[21] This result as well as the lower efficiency of cyclization of Ib in the presence of oxygen shows that the reaction of the intermediates (X) with oxygen does not lead quantitatively to III. Further studies are indicated to elucidate this point.

By sensitization with benzophenone in benzene to reduce reactions of the sensitizer with the solvent, we obtained the quantum yield of cyclization of the triplet of Ia. Its magnitude ($\phi_{TX} = 0.58$) is surprisingly high considering that very inefficient triplet cyclization of structurally similar compounds had been reported.[4,6] In addition we had anticipated a deactivation of the triplet state by the "free rotor effect" which, for example, suppresses the acyclic di-π-methane rearrangement by the triplet state.[24] The cyclization here originating from the triplet state perhaps occurs from an intermediate of the isomerization, viz., the twisted double bond.

The quantum yield of sensitized cyclization reported has been extrapolated to infinite concentration of Ia since the energy transfer rate constant is $\sim 1/50$ of the diffusion rate[25] ($k_t = 3.4 \times 10^8$ s^{-1} M^{-1}). This low energy transfer constant indicates a higher energy of the Franck–Condon triplet state of Ia than calculated from the phosphorescence spectra. This is consistant with a different geometry for the ground state and the excited state with the latter closer to planarity. The same phenomena was observed and rationalized by Wagner[26] for the energy transfer from the benzophenone triplet to diphenyl

and by Swenton[27] for the photocyclization of 2-biphenyl isocyanates. Benzophenone and even acetone do not sensitize the formation of IIb; this result might arise from a fast deactivation of the triplet state or more probably from a relative position of the methylene and the fluorenyl groups that is unfavorable for reaction in the triplet state. This is in complete contrast with the relative reactivity of the singlets of Ia,b. These results taken together show a different geometric requirement, for the same reaction, according to the multiplicity of the reactive states just as expected if the two following mechanisms occur: a concerted singlet cyclization by a planar transition state and a triplet pathway by a twisted methylene double bond. Swenton[28] has recently made the same proposal for the cyclization of 5,5-diphenylcyclohepta-1,3-diene.

Padwa[4] has observed a much lower efficiency of photocyclization for 2,2'-divinylbiphenyl (Id) ($\phi_{S_1} = 0.042$, $\phi_{T_1} = 0.003$) and Laarhoven[6] for some 2,2'-(2-substituted vinyl)-biphenyl (Ie) ($\phi_{S_1} \lesssim 0.003$).

The increased efficiency of the singlet cyclization of Ia,b relative to Id,e can be attributed to more favorable electronic and steric interactions. The electronic effect is reflected by the high value of ΣF^*, the sum of the free valence indexes in the first excited state at the two positions which become bonded during the cyclization, viz., 1.727 for Ia and 1.723 for Ib[3] to be compared with 1.454 for Id and 1.2 for Ie.[6] The absence of substituent at the position 2 of the vinyl group allows a near-planar geometry of the excited state. This accords with the predictions of theoretical calculations for biphenyl[29] and should favor the cyclization. The high efficiency of the photocyclization of Ia can explain that 2,2'-bis(1-phenylvinyl)biphenyl did not give any intramolecular [2 + 2] cycloaddition.

Of special note is the much higher quantum yield for cyclization in the sensitized irradiation compared to the direct photolyses of Ia. This is in contrast with the result of Padwa[4] and Laarhoven[6] on structurally similar compounds but these authors used benzophenone as sensitizer and did not extrapolate ϕ_{sens} at infinite concentration of the biphenyl so the quantum yield measured is perhaps not the true quantum yield of cyclization through the triplet. In fact, Swenton[27] observed, by using a high-energy sensitizer (acetone), a much higher quantum yield of cyclization for sensitized 2-biphenylyl isocyanates than for the case of direct irradiation.

The very low quantum yield of cyclization which arises from the triplet state by direct irradiation can be ascribed to a low intersystem crossing efficiency. For Ia, $\phi_{ST} = 0.03/0.58 \simeq 0.05$. This value is in the range of those reported by Swenton[27] for several 2-substituted biaryl systems.

The detailed discussion of all the deactivation paths will be included in the companion paper.[21]

Comparative Reactivity of the Singlet and the Triplet States for Photocyclization. The observation that the quantum yield of cyclization ($\phi_{II} + \phi_{III}$) in the presence of iodine, which traps the primary product of the photocyclization, is the same as ϕ_{II} in absence of iodine gives a clear indication of the irreversible formation of Xa,b. Since each intermediate (X) formed gives II with a quantum yield of 1 whatever the rate of the hydrogen transfer we can calculate the cyclization rate constant, k_X, from the quantum yield and the lifetime of each reactive state; i.e., $k_X = \phi/\tau$ if the states we have measured the lifetime give in one step the intermediate X.

$$\text{Ia: } k_{SX} = 5.2 \times 10^7 \text{ s}^{-1}$$

$$k_{TX} = 3.3 \times 10^5 \text{ s}^{-1}$$

$$\text{Ib: } k_{SX} = 1.3 \times 10^8 \text{ s}^{-1}$$

The increased singlet reactivity of Ib vis-à-vis Ia is certainly related to its more rigid geometry, which is relatively more favorable (since quasi-planar) for a concerted cyclization than

for other deactivation paths. The reactivity of the triplet state of Ia is lower than that of the singlet state; its higher efficiency of cyclization proceeds simply from its lower deactivation paths. If the triplet cyclization of Ia occurs mainly from the twisted double bond, then the cyclization rate constant from the spectroscopic triplet ($\tau = 1.75 \times 10^{-6}$ s,) would even be considerably less than the value of k_{TX} reported above.

Experimental Section

1. Equipment for Physical Measurements. Melting points were taken with a Kofler block and are uncorrected. Centesimal analyses were performed at the CNRS microanalysis center. All the spectroscopic data are consistent with the proposed formulas. NMR spectra were measured at 60 MHz using Me$_4$Si as internal standard. UV spectra were determined with a Beckman DK 2 A recording spectrometer. The IR spectrometer was a Perkin-Elmer 457 and the mass spectrometer an AEI Model MS-12; the mass spectra were taken at 70 eV.

Fluorescence spectra were obtained with a Hitachi Perkin-Elmer MPF 3 fluorimeter; the spectra were not corrected.

2. Determination of the Reaction Quantum Yields. For the direct irradiations the measurements were made with an optical bench equipped with a Philips spectral low-pressure mercury lamp and interferential filter (MTO intervex) to select the 254-nm wavelength. A similar setup was used for determination of the quantum yields of the sensitized reactions at 366 nm obtained from a high-pressure mercury lamp OSRAM HBO 200 W in a Schoeffel box type 101. The 366-nm wavelength was selected by using an aqueous solution of CuSO$_4$·5H$_2$O (80 g L^{-1}) and an optical filter (MTO A 371 b).

The amount of the products formed was measured from VPC after 5–10% conversion. The light intensity was measured by using the ferrioxalate actinometry[18] in the modification described by Demas.[19]

3. Preparation of the Starting Materials. Only the preparation of unknown compounds is reported.

1-(4-Fluorenyl)-1-phenylethylene (Ib). A Grignard reagent was prepared from 3.83 g (0.027 mol) of methyl iodide, 0.6 g (0.027 mol) of magnesium, and 50 mL of anhydrous ether. To this solution, cooled in an ice bath, was added dropwise a solution of 5.8 g (0.022 mol) of 4-benzoylfluorene in 50 mL of ether, with stirring for 2 h. The mixture was poured into water with 25 mL of concentrated hydrochloric acid. The resulting oil was isolated by a conventional procedure; 50 mL of CCl$_4$ and 8 g of P$_2$O$_5$ were added and the mixture was heated under reflux for 1 h. It was then filtered and Ib was isolated by chromatography on an alumina column. Elution with petroleum ether, followed by a crystallization from ethanol, produced 3.5 g of small, white crystals: yield 60%; mp 76 °C; IR ν_{max} (KBr) 3085, 1445, 1392, 1187, 1029, 905, 790, 780, 740, 718, and 590 cm^{-1}; NMR δ (CCl$_4$) 5.2 (1 H, s), 5.8 (1 H, s), 3.7 (2 H, s), 6.7–7.7 (11 H, m); UV λ_{max} (log ϵ) in cyclohexane 213 (4.14), 240 (3.79), 257.5 (3.90), 268 (3.84), 280 (3.65), 288 (3.45), 300 (3.30).

Anal. Calcd for C$_{21}$H$_{16}$: C, 94.03; H, 5.97. Found: C, 93.94; H, 5.99.

4-Benzoylphenanthrene. A mixture of 1.3 g (0.006 mol) of phenanthrene-4-carboxylic acid and 10 mL of thionyl chloride was refluxed for 3 h. The excess of thionyl chloride was removed by distillation. The acid chloride was obtained by vacuum distillation. A solution of the Grignard reagent from 0.94 g (0.006 mol) of bromobenzene, 0.15 g (0.006 mol) of magnesium, and 30 mL of ether was added to the solution of the acid chloride in 75 mL of benzene cooled by an ice bath. After the mixture had stood at room temperature for 15 h, it was treated with 150 mL of 10% aqueous sodium hydroxide. The organic layer was dried and chromatographed on a column of silica gel. Elution with benzene gave a pale yellowish oil (0.94 g, pure by TLC) which could not be crystallized from many solvents. However, the IR spectrum revealed the presence of a carbonyl group at 1665 cm^{-1}: yield 55%; NMR δ (CCl$_4$) 7.87–8.17 (1 H, m), 6.81–7.77 (13 H, m); UV λ_{max} (log ϵ) in EtOH 208 (4.62), 221 (4.48), 251.5 (4.79), 285 (4.22), 296 (4.15), 349 (3.03).

1-(4-Phenanthryl)-1-phenylethylene (Ic). This compound was synthesized from 4-benzoylphenanthrene by the method of Cainelli.[30]

To a magnesium amalgam (0.16 g (0.0064 mol) of magnesium turnings and 11.2 g (0.0256 mol) of mercury), a solution of 4-ben-

zoylphenanthrene (0.9 g, 0.0032 mol) and 0.86 g (0.0032 mol) of methylene iodide was added dropwise with stirring.

The mixture was refluxed for 3 h and hydrolyzed with ammonium chloride solution. After we proceeded in the usual manner, the oil was chromatographed on an alumina column. Elution with petroleum ether gave 0.5 g of an oil, crystallization of which was unsuccessful using several solvents: yield 28%; IR ν_{max} 2840, 2910, 3040, 1500, 830, 796, 775, and 725 cm^{-1}; NMR δ (CCl$_4$) 5.33 (1 H, s), 5.82 (1 H, s), 6.83–7.83 (13 H, m), 8.68–8.97 (1 H, m); UV λ_{max} (log ϵ) in cyclohexane 223 (4.04), 255 (4.31), 286.5 (3.71), 299 (3.11).

Dehydrogenation of Photoproducts. IIa–c were dehydrogenated to IIIa–c by 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ)$_5$. A mixture of IIa–c and DDQ in dry benzene was heated under reflux for 5 h. The products were purified by chromatography on an alumina column and eluted with benzene.

9-Phenylphenanthrene (IIIa). IIIa (0.119 g) was obtained from 0.127 g of IIa: yield 94%; mp 104–104.5 °C (from ethanol); NMR δ (CCl$_4$) 8.27–8.58 (2 H, m), 6.87–7.83 (12 H, m); UV λ_{max} (log ϵ) in EtOH 250 (4.53), 255 (4.58), 289 (3.84), 297 (3.90).

9-Phenyl-4,5-methylenephenanthrene (IIIb). IIIb (0.192 g) was obtained from 0.200 g of IIb: yield 91%; mp 90–91 °C (from ethanol); IR ν_{max} (KBr) 3080, 1440, 888, 878, 810, 775, 760, 732, 715, 700, and 595 cm^{-1}; NMR δ (CCl$_4$) 4.10 (2 H, s), 7.12–7.80 (12 H, m); UV λ_{max} (log ϵ) in cyclohexane 230 (4.47), 257 (4.72), 304 (4.07), 330 (3.15).

Anal. Calcd for C$_{19}$H$_{14}$: C, 94.74; H, 5.26. Found: C, 94.31; H, 5.91.

4-Phenylpyrene (IIIc). IIIc (0.075 g) was obtained from 0.079 g of IIc: yield 97%; mp 133 °C (from petroleum ether).

4. Photochemical Reactions. Direct irradiations have been carried out in a Rayonet photochemical reactor at 300 nm.

Ia. A degassed solution of Ia (150 mg, 5.86 × 10^{-4} mol) in 100 mL of cyclohexane was irradiated in a quartz vessel using 300-nm light for 90 min; a single photoproduct was formed. Evaporation of the solvent and recrystallization from ethanol gave 146 mg of IIa (white crystals, mp 84 °C, yield 98%): NMR δ (CCl$_4$) 3.11 (2 H, d, $J = 7.98$ Hz), 4.09 (1 H, t, $J = 7.98$ Hz), 6.65–7.79 (13 H, m).

Ib. Under the same conditions 150 mg of Ib (5.86 × 10^{-4} mol) in 100 mL of cyclohexane was irradiated for 90 min. After evaporation of the solvent a white solid was obtained, the recrystallization of which from ethanol gave 145 mg of IIb: mp 56 °C; yield 98%; NMR δ (CCl$_4$) 3.81 (2 H, s), 3.23 (2 H, d, $J = 8$ Hz), 4.38 (1 H, t, $J = 8$ Hz), 6.58–7.69 (11 H, m); MS *m/e* 268 (molecular peak).

Ic. Under the same conditions 79 mg of Ic (2.8 × 10^{-5} mol) in 50 mL of cyclohexane was irradiated for 15 min.

Evaporation of the solvent gave 79 mg of an oil which could not be crystallized from many solvents: yield 100%; NMR δ (CCl$_4$) 3.46 (2 H, d, $J = 9.6$ Hz), 4.49 (1 H, t, $J = 9.6$ Hz), 6.75–7.85 (13 H, m).

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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 $\tau_f = 4 \times 10^{-9}\,s^{-1}$, respectively. By flash photolysis, two transients species having different lifetimes have been observed. One, whose absorption has a maximum at 370 nm ($\epsilon_{max}\ (1.7 \pm 0.3) \times 10^4\,M^{-1}\,cm^{-1}$), with a decay time on the order of 1 μs, is scavenged by oxygen ($k_Q = 1.0 \times 10^9\,M^{-1}\,s^{-1}$). It has been assigned to the triplet state. The second one, absorbing in the visible (λ_{max} 510 nm, $\epsilon_{max}\ (1.2 \pm 0.2) \times 10^4\,M^{-1}$ cm^{-1}) and below 300 nm, has a lifetime of the order of 1 ms. It is scavenged by oxidizing agents such as iodine ($k_{I_2} = 4.5 \times 10^6$ $M^{-1}\,s^{-1}$) 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
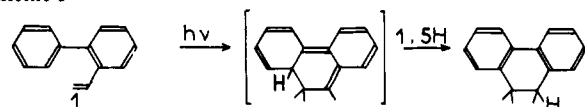
Scheme II
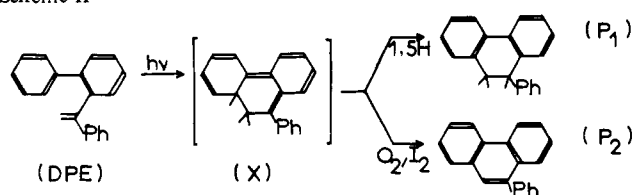
II. Experimental Section

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 neodynium 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]