Photochemistry of Phenylimidazoles

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The photochemical formation of 9,10-phenanthroimidazole from 4,5-diphenylimidazole and 2-phenyl-9,10-phenanthroimidazole from 2,4,5-triphenylimidazole have been studied with 313-nm excitation in different solvents. Noteworthy is the observation that no dihydrophenanthrene intermediate could be detected and that the photocyclization proceeds in air-saturated as well as in degassed solutions. The quantum yields for the formation of 9,10-phenanthroimidazole are generally an order of magnitude larger in air-saturated than in degassed solutions. The process proceeds through the singlet state and the quantum yield for the cyclization reaction in degassed acetonitrile solutions for 4,5-diphenylimidazole and 2,4,5-triphenylimidazole is $0.91 \pm 0.1 \times 10^{-3}$ and $0.57 \pm 0.07 \times 10^{-3}$, respectively. The luminescence spectra and quantum yields for 4,5-diphenylimidazole and its photoproduct have also been measured.

Introduction

The photocyclization of stilbene and its analogs to phenanthrene type molecules has been a subject of continuing interest.[1-4] The formation of the yellow colored 4a,4b-dihydrophenanthrene intermediate has been demonstrated in the photocyclization of *cis*-stilbene and its analogs to phenanthrenes, and the formation of hydrogen peroxide has been shown to arise from the reaction between oxygen and dihydrophenanthrene. In a degassed solution the yellow color disappears and the system reverts back to *cis*-stilbene.[5] Although it has been shown that the cyclization of *cis*-stilbene proceeds *via* the π,π^* singlet state,[6] the mechanism by which the dihydrophenanthrene intermediate is converted to the corresponding phenanthrene continues to be a source of controversy. Recently, Srinivasan and Hsu[7] suggested a free-radical process which leads to either 9,10-dihydrophenanthrene or directly to the corresponding phenanthrene, depending upon whether the termination step involves a gain or loss of a hydrogen atom. In fact, they report that the 313-nm irradiation of a degassed solution of α-phenylcinnamic acid in methanol leads directly to the 9-phenanthroic acid in the absence of any oxidizer.

In view of the continuing interest in photocyclizations and the unresolved problem concerning dihydrophenanthrene we have investigated the photochemistry of 4,5-diphenyl- and 2,4,5-triphenylimidazole at 313 nm in four different solvents, in air-saturated and degassed solutions. In addition to measuring the photochemical quantum yields, the luminescence spectra and quantum yields have also been measured.

Experimental Section

Materials. 4,5-Diphenyl- and 2,4,5-triphenylimidazole were obtained from Aldrich Chemical Co. and recrystallized prior to use. The former was recrystallized as white needles (mp 232–233°) from benzene and the latter was recrystallized from dilute ethanol as a white powder (mp 273–274°). Zone-refined benzophenone from J. Hinton was used as a triplet sensitizer and *cis*-1,3-pentadiene from Chemical Samples Co. as a triplet quencher. Spectrograde acetonitrile, EPA, and hexane were used as received from Matheson Coleman and Bell.

9,10-Phenanthroimidazole was prepared by refluxing 9,10-diaminophenanthrene with an equivalent amount of formic acid in xylene, and the white product obtained in low yield was recrystallized from dilute ethanol water solutions. The uv spectrum and the melting point (303–304°) agree satisfactorily with the literature.[8]

Apparatus. Small scale photolyses were performed in 1-cm quartz spectrophotometric cells, connected by a graded seal to a vacuum system (10^{-4} mm), and sealed off after degassing. Excitations at 285 and 313 nm were isolated from an Osram HBO 100W/2 high-pressured mercury lamp with 10-nm half-bandwidth interference filters. The ferrioxalate actinometer[9] was used to measure light intensities, which were typically 1.4×10^{15} quanta/sec. Large-scale photolyses were performed at concentrations of approximately 10^{-3} *M*,

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(1) K. A. Muszkat and A. Fischer, *J. Chem. Soc. B*, 662 (1967).

(2) F. R. Stermitz in "Organic Photochemistry," Vol. I, O. L. Chapman, Ed., Marcel Dekker, New York, N. Y., 1967, p 247.

(3) M. Scholz, F. Dietz, and M. Mühlstadt, *Z. Chem.*, **7**, 329 (1967).

(4) A. V. Blackburn and C. J. Timmons, *Quart. Rev., Chem. Soc.*, **23**, 482 (1969).

(5) W. M. Moore, D. D. Morgan, and F. R. Stermitz, *J. Amer. Chem. Soc.*, **85**, 829 (1963).

(6) F. B. Mallory, C. S. Wood, and J. T. Gordon, *ibid.*, **86**, 3094 (1964).

(7) R. Srinivasan and J. N. C. Hsu, *ibid.*, **93**, 2816 (1971). There are two dihydrophenanthrenes which can occur during the degassed photocyclization of stilbene and its analogs, *i.e.*, 4a,4b-dihydrophenanthrene and 9,10-dihydrophenanthrene. The former is produced with stilbene while the latter has been observed in certain stilbenes containing one or more electron-withdrawing substituents on the central double bond.

(8) R. Epsztein, *Mem. Serv. Chim. Etat. (Paris)*, **36**, 353 (1951).

(9) C. H. Hatchard and C. A. Parker, *Proc. Roy. Soc., Ser. A*, **235**, 518 (1956).

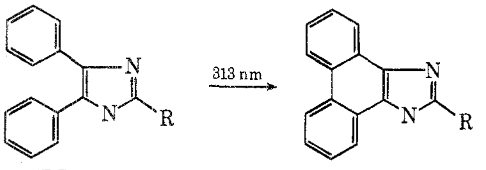
using a 450-W Hanovia medium-pressure lamp and a Pyrex sleeve to limit the incident wavelength region to values greater than 280 nm. Nitrogen gas was continuously bubbled through the solution during the large-scale runs.

Analytical Procedures. The disappearance of 4,5-diphenyl- and 2,4,5-triphenylimidazole was followed quantitatively at 254 and 262 nm, respectively, with a Beckman DU spectrophotometer. The following molar extinction coefficients were used at 254 nm: 9.0×10^3 for the diphenylimidazole and 77×10^3 for 9,10-phenanthroimidazole, and at 262 nm: 8.0×10^3 for triphenylimidazole and 56×10^3 for 2-phenyl-9,10-phenanthroimidazole. Uv spectra were recorded with a Bausch and Lomb Model 505 spectrophotometer. Flourescence and phosphorescence spectra were obtained with an apparatus described elsewhere,[10,11] and were not corrected for the variation of sensitivity of the photomultiplier–monochromator combination with wavelength.

The photoproduct was separated by thin layer chromatography (Eastman Kodak or Brinkman Instruments thin layer plates with fluorescent indicator) using three different solvent systems: ethyl acetate, acetone, and 90% hexane–10% ethanol. The photoproduct from the 4,5-diphenylimidazole photolysis was obtained, following large scale photolysis, by flash evaporation and identified by the usual spectroscopic methods and by comparison with an authentic sample of 9,10-phenanthroimidazole. Fractional sublimation was found to be a convenient method for the separation of phenanthroimidazole from the diphenylimidazole.

Results

Our initial interest in the photoexcitation of 4,5-diphenylimidazole (DPI) arose from the observation that its fluorescence in 0.1 *M* NaOH decreased with time. Figure 1 illustrates the change of fluorescence intensity occurring with 285-nm excitation. Large scale photolyses were used to determine that the photochemistry of DPI leads to 9,10-phenanthroimidazole (PI) and similarly that 2,4,5-triphenylimidazole (TPI) leads to 2-phenyl-9,10-phenanthroimidazole (PPI), *i.e.*



(DPI, TPI)
R = H, C_6H_5

(PI, PPI)

Identification of the photoproduct was made by using uv, ir, and thin layer chromatography and by comparison with an authentic sample. It was observed that in 0.1 *M* NaOH a side reaction occurs which complicates the photochemistry; consequently, quantitative photolyses were performed in its absence. The photocyclization of DPI in solvents such as ethanol, 97% hexane–3% ethanol, 70% water–30% ethanol, and acetonitrile proceeds without any detectable side reaction.

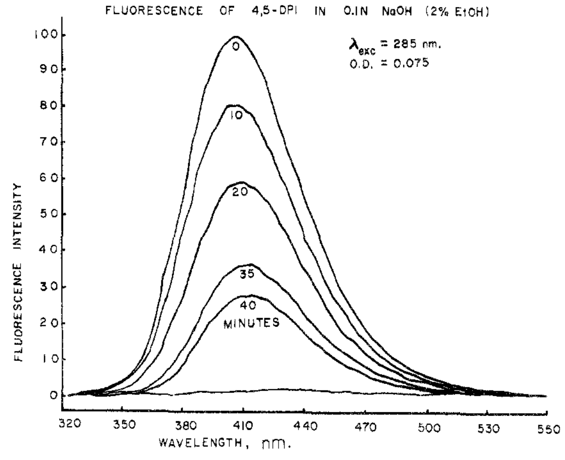


Figure 1. Time dependence of the fluorescence of 4,5-diphenylimidazole in 0.1 *M* NaOH (2% ethanol) excited at 285 nm.

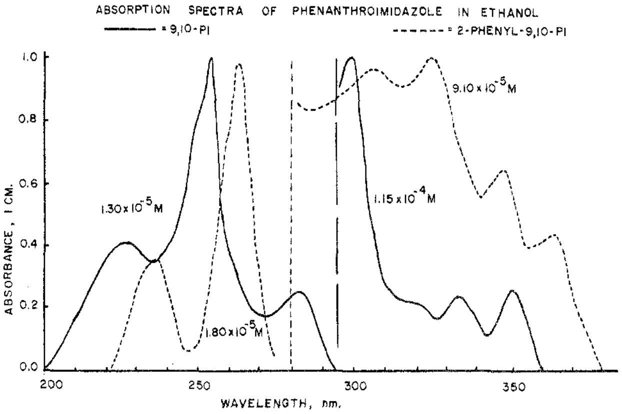


Figure 2. Absorption spectrum of 9,10-phenanthro- and 2-phenyl-9,10-phenanthroimidazole in ethanol, resulting from the photochemistry of 4,5-diphenyl- and 2,4,5-triphenylimidazole, respectively.

The photochemical formation of PI from DPI and PPI from TPI is very well suited for a spectrophotometric determination of the quantum yields, since in most solvents the photochemistry proceeds very cleanly, *i.e.*, DPI → PI and TPI → PPI. In each of the two systems studied, the product formed does not undergo further photochemistry. During the photochemistry of DPI the appearance of the photoproduct PI is manifested by five well-defined peaks in the uv spectrum which agree with the following reported absorption peaks and molar extinction coefficients of 9,10-phenanthroimidazole: 254 (7.7×10^3), 282 (1.1×10^3), 300 (8.8×10^3), 324 (sh), 334 (1.5×10^3), and 351 nm (2.0×10^3).[8] The absorption spectrum of the ob-

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[10] A. Weisstuch and A. C. Testa, *J. Phys. Chem.*, **72**, 1982 (1968).

[11] M. O'Sullivan and A. C. Testa, *J. Amer. Chem. Soc.*, **92**, 258 (1970).

served photoproducts, PI and PPI, are presented in Figure 2.

The quantum yield results in air-saturated and degassed solutions for the photocyclization of DPI with 313-nm excitation are presented in Table I. It is evident that in all cases the quantum yield is very small, but significantly larger in the air-saturated runs. Stegemeyer[12] has reported a value of $\Phi = 0.07$ for the photochemical formation of phenanthrene from *cis*-stilbene in aerated hexane at 25°. Of particular interest in the present investigation is the result that the yellow dihydrophenanthrene intermediate was never observed during the photolysis of DPI, and that the presence of air is not necessary for the formation of 9,10-phenanthroimidazole.

Table I: Photochemical Quantum Yields for the Formation of 9,10-Phenanthroimidazole from 4,5-Diphenylimidazole[a]

Solvent	I_a, quanta/sec	Photolysis time, min	$\Phi_{deg} \times 10^3$	$\Phi_{air} \times 10^3$
Acetonitrile	1.60×10^{15}	100–300	0.91 ± 0.1	4.3 ± 0.2
70% water–30% ethanol	1.32×10^{15}	200–800	0.47 ± 0.05	4.7 ± 0.9
Ethanol	1.30×10^{15}	100	0.46	2.0
97% hexane–3% ethanol	1.40×10^{15}	75–200	0.30	6.9

[a] λ_{exc} 313 nm; concentration 7–8 × 10^{-5} *M*.

In the aerated photolysis of TPI the sum of the concentration of the cyclized product and unreacted TPI was considerably less than the initial TPI concentration indicating that some additional photoreaction occurs in the presence of oxygen. Investigations performed by Dufraisse[13] and White[14] indicate that TPI forms a peroxide upon uv irradiation in aerated solution. Consequently, quantum yields for this molecule were determined only in degassed solutions, where the reaction proceeds without side effects. A summary of the results are given in Table II. It is seen that the quantum yields for TPI are ~10^{-3} in each of the three solvent systems studied. This photocyclization occurs in degassed solutions without any evidence of the dihydrophenanthrene intermediate as was the case with DPI photochemistry. An unexpected result was that the photochemistry of TPI in degassed diethyl ether does not lead to the phenanthroimidazole, while DPI under the same conditions does.

It has been demonstrated that the photocyclization of *cis*-stilbene proceeds *via* its lowest excited singlet state, and in general this has been true in analogs of stilbenes.[1-4] In the present study we attempted to deduce the nature of the reactive state by using *cis*-piperylene as a triplet quencher and benzophenone as a triplet sensitizer. A degassed solution of 7.8 × 10^{-5} *M* DPI in 97% hexane–3% ethanol with 0.2 *M* *cis*-piperylene irradiated at 313 nm for 1020 min did not lead to any significant change in the quantum yield for the formation of PI. In addition, the fluorescence of DPI was unaffected by the presence of added *cis*-piperylene. PI was not formed in degassed acetonitrile solutions when DPI was sensitized by triplet energy transfer from benzophenone ($E_T = 69.0$ kcal/mol). The excited singlet state energy of DPI was estimated to be 87 kcal/mol from the mirror image plots of its absorption and fluorescence spectrum, and the triplet state energy, estimated from its phosphorescence spectrum in EPA at 77°K, is 67 kcal/mol. The approximate one order of magnitude increase in the quantum yield for air-saturated solutions relative to degassed solutions tends to rule out a triplet mechanism. In view of the above results it appears that the photocyclodehydrogenation of DPI proceeds from the lowest excited π,π^* singlet state. It is somewhat more difficult to elucidate the photoreactive state in TPI photochemistry because of enhanced and undetermined photochemistry in the presence of 0.2 *M* *cis*-piperylene; however, the similarity of the process with DPI and the increased quantum yields in air-saturated solutions suggest a singlet state reaction.

Table II: Photochemical Quantum Yields for the Formation of 2-Phenyl-9,10-phenanthroimidazole from 2,4,5-Triphenylimidazole in Degassed Solutions[a]

Solvent	I_a, quanta/sec	Photolysis time, min	$\Phi \times 10^3$
Acetonitrile	1.20×10^{15}	100	0.57 ± 0.07
Ethanol	1.10×10^{15}	65–200	2.2 ± 0.2
99.5% hexane–0.5% ethanol	1.40×10^{15}	120	2.2 ± 0.3

[a] λ_{exc} 313 nm; concentration 3–4 × 10^{-5} *M*.

In this photochemical investigation the fluorescence and phosphorescence spectra of 9,10-phenanthroimidazole are reported for the first time. The fluorescence yield in ethanol, relative to a value of 0.09 for *d,l*-tryptophan,[15] was determined to be 0.35 and its phosphorescence yield in EPA at 77°K was estimated to be 0.08 relative to a value of 0.90 for benzophenone.[16] The fluorescence yield of DPI in ethanol was determined to be 0.09, while in 0.1 *M* NaOH, $\Phi_F = 0.68$. This significant increase of fluorescence in a basic

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(12) H. Stegemeyer, *Z. Naturforsch.*, **176**, 153 (1962).

(13) C. Dufraisse, A. Etienne, and J. Martel, *C. R. Acad. Sci.*, **244**, 970 (1957).

(14) A. White and M. Harding, *Photochem. Photobiol.*, **4**, 1129 (1965).

(15) V. G. Shore and A. B. Pardee, *Arch. Biochem. Biophys.*, **60**, 100 (1956).

(16) N. J. Turro, "Molecular Photochemistry," W. A. Benjamin, New York, N. Y., 1965, p 75.

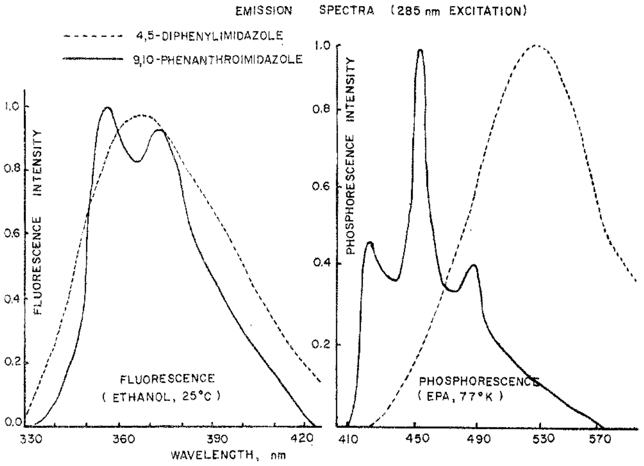


Figure 3. Fluorescence and phosphorescence spectra of 4,5-diphenylimidazole and 9,10-phenanthroimidazole obtained with 285-nm excitation.

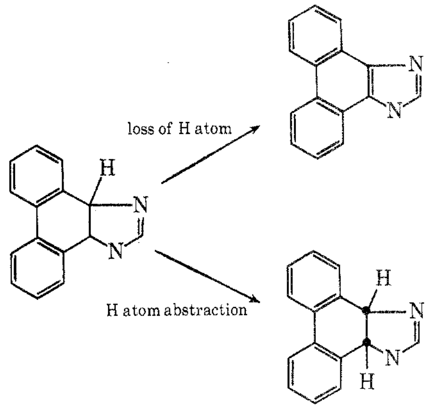
medium is due to the formation of the anion.[17] The phosphorescence yield of DPI in EPA was determined to be 0.02 relative to benzophenone. The fluorescence and phosphorescence spectra of 4,5-diphenylimidazole and its photoproduct, 9,10-phenanthroimidazole, are presented in Figure 3. Noteworthy is the observation that there is increased structure in the fluorescence and phosphorescence spectrum of PI relative to DPI, which may be related to the restricted motion of the phenyl rings in forming the photoproduct.

Discussion

The photocyclization of stilbene and its analogs to phenanthrene type compounds is generally accepted to occur *via* a dihydrophenanthrene intermediate, which is air oxidized to the phenanthrene.[1] In the present investigation we have been unable to observe any evidence for the dihydrophenanthrene intermediate during the degassed photolyses of DPI and TPI; consequently, it appears that the formation of the phenanthroimidazoles can occur directly from the phenylimidazoles without any oxidizer.

The formation of PI from DPI is enhanced by a factor of 20, relative to degassed runs, when photolyzed in air-saturated hexane–ethanol solutions; however, it is very unlikely that sufficient dissolved molecular oxygen exists in degassed solutions, at the concentrations needed for the amount of phenanthroimidazole formed. When degassed samples of DPI and TPI were opened to the atmosphere after photolysis no additional phenanthrene was formed. Moore, *et al.*,[5] Mallory, *et al.*,[6] and Fisher[1] postulate that oxygen is required to oxidize the 4a,4b-dihydrophenanthrene intermediate, formed by irradiation, to the corresponding phenanthrene. Moore, *et al.*,[5] have reported that 0.92 mol of oxygen are consumed for each mole of phenanthrene formed. This type of oxidation does not appear to be operative in the photocyclization of DPI.

Srinivasan and Hsu[7] recently demonstrated solvent effects on the photocyclization of stilbene as an indication of a free-radical mechanism, which appears to be a factor in the photochemistry of DPI and TPI. Although we are unable to account for the loss of hydrogen atoms in forming the phenanthrene compounds, a hydrogen abstraction involving the solvent, followed by cyclization and aromatization, as suggested by Srinivasan and Hsu,[7] could lead to formation of a species, which either loses a hydrogen atom to produce the phenanthroimidazole or undergoes a hydrogen abstraction process to form 9,10-dihydrophenanthroimidazole, *i.e.*



The absence of the dihydrophenanthrene intermediate during the degassed photolysis of DPI and TPI in this investigation suggests that the process involving loss of an H atom predominates. A more definitive mechanism, however, for the loss of hydrogen atoms during the photochemistry of phenylimidazoles and other analogs of stilbene still needs to be elucidated.

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(17) H. Walbe and R. Isensee, *J. Org. Chem.*, **26**, 2789 (1961), report $pK_a = 12.80$ for the loss of the proton attached to the pyrrole nitrogen.