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Photocyclization of 1,2-Bispyrazylethylene and 2-Styrylpyrazine

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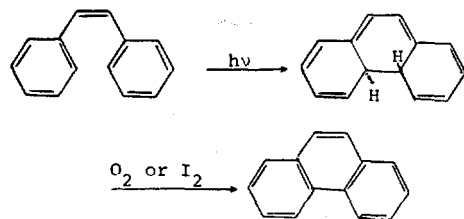
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1,4,5,8-Tetraazaphenanthrene, a new tetraazaheteroaromatic compound, has been synthesized photochemically in 90% yield and quantum yield of 5.1×10^{-2} from dilute benzene solutions of 1,2-bispyrazyl ethylene (BPE) in the presence of oxygen as an oxidant. Iodine was not appropriate oxidant because of strong complexing with BPE and also enhanced intersystem crossing of BPE and thereby decreasing the photocyclization of BPE. Salt effect, solvent effect, and quenching and sensitization studies on the photocyclization of BPE have shown that $^1(n, \pi^*)$ is the reactive state for the cyclization in comparison to $^1(\pi, \pi^*)$ state for the ordinary stilbene derivatives.

Introduction

The oxidative photodehydrocyclization of stilbenes, substituted stilbenes, other 1,2-diaryl-substituted ethylenes generally proceeds by the partial steps of conrotatory ring closure as predicted by the Woodward-Hoffmann rule for a concerted photocyclization of 1,3,5-hexatrienes in the S_1 state followed by oxidation of thus formed dihydrophenanthrenes. For the cyclization to occur, the sum of the free valence indices ($\sum F^*$) for the first excited state at atoms between which the new bond is formed must be greater than unity. This elegant method has proved to be the efficient method to synthesize phenanthrenes and over 100 phenanthrenes have been synthesized by this method¹⁻⁹.



This type of photodehydrocyclization reaction has also been extensively used for the synthesis of chrysene derivatives and has proved to be the best method for the synthesis of helicenes¹⁰. The synthesis of azaphenanthrenes by classical methods is very difficult and most of the time failed⁷. The synthesis of 1,4,5,8-tetraazaphenanthrene, a new tetraazaheteroaromatic compound, is attempted by the oxidative photocyclization of 1,2-bispyrazylethylene (BPE), one of the nitrogen containing stilbene analogues.

In BPE, $^1(n, \pi^*)$ state has about the same energy as $^1(\pi, \pi^*)$ state and consequently extensive mixing between these two states results obscuring $n-\pi^*$ band¹¹. Because of the (n, π^*) excited states, BPE shows quite different photoche-

mical behavior from the ordinary stilbenes such as photoreduction¹² and photoaddition to tetramethylethylene¹³ through the $^1(n, \pi^*)$ states. Thus, the mechanism of the photocyclization reaction is also expected to be different from that of the stilbenes and the subject will be investigated along with the photocyclization of 2-styrylpyrazine.

Experimental

Materials. All the solvents such as benzene, cyclohexane, ethanol, *t*-butanol, and acetonitrile were purified immediately prior to use by the known standard methods¹⁴. Benzophenone (Merck) was recrystallized three times from cyclohexane (m.p. 46°C). Azulene (Aldrich) was sublimed under vacuum immediately prior to use. Naphthalene (Aldrich) was recrystallized and sublimed under vacuum. Sodium acetate (Wako E.P. Grade) was recrystallized twice from water-ethanol (1:4 v/v) mixed solvent. *Trans*-BPE and *cis*-BPE were synthesized by the method reported¹¹. *Trans*-styrylpyrazine (STP)¹⁵ and *cis*-STP⁸ were synthesized as reported.

Spectra. Nuclear magnetic resonance spectra were measured on a Varian T-60A spectrometer against tetramethylsilane internal standard in deuteriochloroform (BPE) and carbon tetrachloride (STP). Chemical shifts are reported as δ values. Infrared spectra were obtained on a Perkin-Elmer Model 267 spectrophotometer in KBr pellets. UV-VIS spectra were recorded on a Cary 17 spectrophotometer. The mass spectra were obtained at 30 eV on a Hitachi RMU-7M mass spectrometer. Elemental analysis was carried out at the Korea Institute of Science and Technology, Seoul, Korea. Gas chromatograms were obtained on a Varian 2800 series gas chromatograph using FID detector and 6% OV-17 on Chromosorb W packing material in a 6 ft \times 1/8 in copper column.

Synthesis of 1,4,5,8-Tetraazaphenanthrene. *Trans*-BPE (184 mg, 10^{-3} mole) was dissolved in purified benzene (1l) and irradiated in a preparative RPR 208 Rayonet Reactor with 350 nm lamp for 8 hours in a Pyrex vessel. The solution was stirred with a magnetic bar during the irradiation. After irradiation, the solvent was evaporated off with a rotary evaporator and 30 ml of acetone was added to dissolve unreacted BPE. After filtration, the residue was sublimed under vacuum followed by recrystallization from methanol-carbon tetrachloride mixed solvent first, then from benzene-ethanol mixed solvent. The product was also separated by alumina (Wako, neutral, activity I) column chromatography utilizing benzene-methylene chloride (1:1 v/v) eluent. A 50 cm \times 1.5 cm column was packed with alumina to a height of 35 cm. The product was eluted first followed by *trans*- and then *cis*-BPE.

Quantum Yield Measurements. Solutions (5 ml) of BPE and STP with or without quenchers, sensitizers, and alkaline salts were put into clean 13 \times 100mm Pyrex tubes and irradiated in a "merry-go-round" unit with a 450 W Hanovia medium pressure mercury arc lamp. A Corning glass filter #7-54 and a solution filter of 2.5×10^{-3} M potassium dichromate in 1% sodium carbonate aqueous solution were used to get 313 nm monochromatic light. Corning glass filters #7-37 and #0-52 were employed to get 366 nm monochromatic light. Ferrioxalate actinometry¹⁶ was used to measure the light intensity and the quantitative analysis was carried out with a gas chromatograph.

Results and Discussion

Identification of the Photoreaction Product. The irradiation product of BPE was isolated by column chromatography and purified by sublimation prior to characterization.

The compound has a sharp melting point of 244°C and the structure of the product was determined to be 1,4,5,8-tetraazaphenanthrene, the photodehydrocyclization product, by elemental analysis and various spectral data. The mass spectra (Figure 1) show the *m/e* 182 peak which corresponds to the molecular ion peak of 1,4,5,8-tetraazaphenanthrene and the peak is the base peak indicating the aromatic character of the compound. The fragmentation pattern shows *m/e* 155 peak which is M-HCN and the 128 peak represents M-2HCN which are all characteristic of nitrogen heteroaromatic compound.

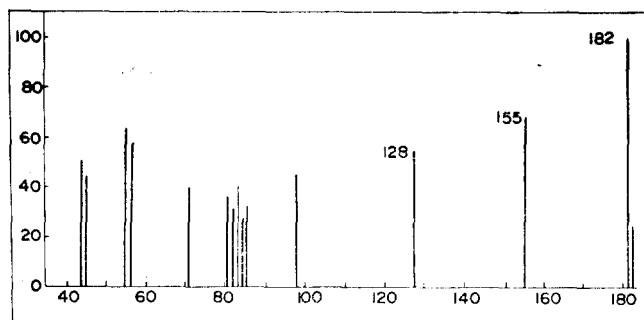


Figure 1. Mass spectrum of 1,4,5,8-tetraazaphenanthrene.

The elemental analysis is consistent with the molecular formula, $C_{10}H_6N_4$ (182.2).

Calc.	C 65.93	H 3.30	N 30.77
Found	65.5	3.4	31.3

The infrared spectra show a characteristic aromatic ν_{C-H} band at 3030 cm^{-1} and the out-of-plane δ_{C-H} of *cis* and *trans* olefins at 725 and 975 cm^{-1} disappeared along with the monosubstituted pyrazine ring peaks. The 1H nuclear magnetic resonance spectra ($CDCl_3$) show δ 8.3 (s, 2H), 9.06 (d, 2H, $J=2$ Hz), and 9.15 (d, 2H, $J=2$ Hz) peaks which are consistent with the 1,4,5,8-tetraazaphenanthrene. The absorption spectra show strong new λ_{max}^{OH} at 280 nm ($\epsilon 3 \times 10^4$) and at 215 nm ($\epsilon 3 \times 10^4$) indicating the compound to be aromatic.

The photoproduct of STP was isolated by column chromatography and characterized to be 1,4-diazaphenanthrene by the nuclear magnetic resonance spectra which were consistent with the literature value¹⁷.

Mechanism of the Photocyclization Reaction. The benzene or cyclohexane solutions of BPE give almost 90% yield of 1,4,5,8-tetraazaphenanthrene through oxidative cyclization on irradiation. 1,4-Diazaphenanthrene is also synthesized in good yield by photodehydrocyclization of STP in contrast to the unsuccessful classical methods^{18,19}.

The oxidative photodehydrocyclization of both BPE and STP seems to proceed by the conrotatory ring closure followed by oxidation of thus formed azadihydrophenanthrene derivatives. Neither 1,4,5,8-tetraazaphenanthrene nor 1,4-diazaphenanthrene was obtained when the dilute solutions of BPE or STP (10^{-3} M) were degassed by freeze-pump-thaw cycle and sealed in Pyrex ampoules prior to irradiation. A new broad absorption band around 400-600 nm appeared as in the case of stilbene suggesting the formation of dihydrophenanthrene derivatives. The yellow color of the solution was bleached much more rapidly than that of dihydrophenanthrene when the light source was turned off indicating the thermal ring opening of thus formed azadihydrophenanthrenes is much more efficient than that of dihydrophenanthrene.

The quantum yields of oxidative photodehydrocyclization are tabulated in Table 1. The quantum yield from *cis*-BPE is about 10 times greater than that of *trans*-BPE indicating that the photocyclization occurs from the excited state of *cis*-BPE.

When the reaction is sensitized by benzophenone or naphthalene, quantum yield decreases dramatically for both BPE and STP. Azulene, a good triplet quencher, does not quench the photodehydrocyclization and the photocyclization reaction therefore occurs from the excited singlet state as in the case of stilbene.

The alkaline salt effect and solvent effect on the quantum yields of photodehydrocyclization are shown in Table 2. The quantum yield decreases sharply as the polarity of the solvent or the concentration of the alkaline salt increase as in the case of photoreduction of BPE¹². This indicates the reactive state of the photocyclization to be the (n, π^*) singlet state rather than the (π, π^*) singlet state which is the case for

TABLE 1: Quantum Yields of Oxidative Photodehydrocyclization of BPE and STP

	Conc. of $\phi_2\text{CO}$ (M)	Conc. of azulene (M)	Quantum yield		
			313 nm	366 nm	
<i>cis</i> -BPE			5.1×10^{-2}	1.8×10^{-2}	
	1.0×10^{-2}		4.3×10^{-2}	1.2×10^{-2}	
	2.0×10^{-2}		2.2×10^{-2}	0.5×10^{-2}	
	5.0×10^{-2}		1.5×10^{-2}	0.1×10^{-2}	
		1.0×10^{-3}		4.7×10^{-2}	1.6×10^{-2}
		2.0×10^{-3}		5.4×10^{-2}	1.7×10^{-2}
<i>trans</i> -BPE		3.0×10^{-3}	5.4×10^{-2}	1.8×10^{-2}	
		5.0×10^{-3}	4.6×10^{-2}	2.0×10^{-2}	
			5.8×10^{-3}		
<i>cis</i> -STP			4.8×10^{-3}		
	5.0×10^{-2}		4.7×10^{-3}		
	1.0×10^{-2}		3.8×10^{-3}		
	5.0×10^{-2}		2.7×10^{-3}		
		5.0×10^{-4}		4.0×10^{-3}	
		1.0×10^{-3}		4.3×10^{-3}	
<i>trans</i> -STP		5.0×10^{-3}	4.5×10^{-3}		
			8.3×10^{-4}		

[BPE] : 1.0×10^{-3} M in benzene; [STP] : 5.0×10^{-4} M in benzene.

TABLE 2: Alkaline Salt and Solvent Effect on the Photodehydrocyclization of BPE and STP. λ_{ex} : 313 nm

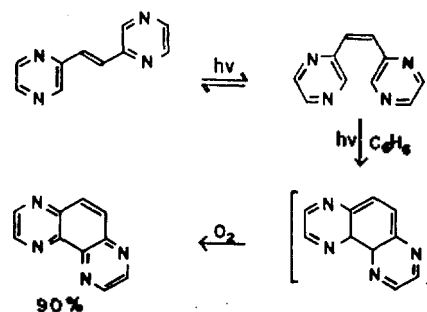
	Solvent	Conc. of NaOAc (M)	Quantum yield
<i>cis</i> -BPE	Ethanol-benzene		2.9×10^{-2}
	2:3 v/v	1.0×10^{-3}	2.3×10^{-2}
	2:3 v/v	2.0×10^{-3}	1.8×10^{-2}
	2:3 v/v	5.0×10^{-3}	0.6×10^{-2}
	Benzene		5.1×10^{-2}
	Cyclohexane		5.2×10^{-2}
	<i>t</i> -Butanol		3.0×10^{-2}
	Ethanol		2.1×10^{-2}
	Acetonitrile		1.8×10^{-2}
	<i>cis</i> -STP	Ethanol-benzene	
Ethanol-benzene			3.2×10^{-3}
Ethanol-benzene		5.0×10^{-4}	3.0×10^{-3}
Ethanol-benzene		1.0×10^{-3}	2.5×10^{-3}
Ethanol-benzene		2.5×10^{-3}	1.1×10^{-3}
Benzene			4.8×10^{-3}
Cyclohexane			4.7×10^{-3}
<i>t</i> -Butanol			3.1×10^{-3}
Ethanol			2.8×10^{-3}
Acetonitrile			2.5×10^{-3}

cis-BPE : 1.0×10^{-3} M; *cis*-STP: 5.0×10^{-4} M.

stilbene.

In conclusion, the photocyclization reaction of BPE and

STP occurs from the lowest excited (n,π^*) singlet state and oxidation of thus formed tetraaza- or diazadihydrophenanthrene gives tetraaza- or diazaphenanthrene in good yields.



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