TABLE 3: Relative Rates of the Photoreaction between Skin-Sensitizers and Pyrimidine Bases

Reaction mixture	Initial rate ΔO.D. $(s^{-1} \times 10^5)$	Relative rate*
Coumarin	1.38	1.5
Coumarin + Thymine	0.90	1.0
Coumarin + Uracil	0.76	0.8
Coumarin + 5-Fluorouracil	1.66	1.8
8-Methoxypsoralen	0.60	0.7
8-Methoxypsoralen + Thymine	0.60	0.7
8-Methoxypsoralen + Uracil	0.68	0.8
8-Methoxypsoralen + 5-Fluorouracil	0.93	1.0
cis-Benzodipyrone	6.73	7.5
cis-Benzodipyrone + Thymine	5.19	5.8
cis-Benzodipyrone + Uracil	0.04	6.7
cis-Benzodipyrone + 5-Fluorouracil	7.93	8.8
trans-Benzodipyrone	48.70	54.1
trans-Benzodipyrone + Thymine	34.10	37.9
trans-Benzodipyrone + Uracil	46.20	51.3
trans-Benzodipyrone + 5-Flurorouracil	54.40	60.4

* Relative to the rate of the coumarin-thymine reaction

photocycloadduct of DMC and 5-FU formed through 2+2 cycloaddition.

The Mechamism of the Photoaddition Reaction of DMC to 5-FU. DMC has no self-quenching effect on fluorescence and fluorescence of DMC was not quenched by 5-FU under the experimental conditions employed. The photocycloaddition reaction of DMC to 5-FU occurs probably via excited singlet state, since DMC has very low efficiency in populating the triplet state ($\Phi_{F_1} = 0.65$ at 298 °K, Φ_P/Φ_{F_1} 0.05 at 77 °K) and the photocyclodimerization of DMC proceeds via excited singlet state exclusively in direct inrradiation.[12] The relative photoreactivity of DMC and other coumarins toward serveral pyrimidine bases[6] and other coumaryl coumpounds[11] were investigated as shown in Table 2 and 3. 5-FU is the most reactive base to excited coumarins. Only exception among many pyrimidine bases tested is 1,3-dimethylthymine.

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Photocycloaddition Reaction of 1,2-Bispyrazylethylene to Tetracyanoethylene

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Benzene solution of trans-1,2-bispyrazylethylene and electron deficient olefin, tetracyanoethylene, as a π-acceptor gave 1,2-bispyrazyl-3,3,4,4-tetracyanocyclobutane, a $2\pi + 2\pi$ cycloaddition product, on irradiation with 350 nm UV light. Fluorescence studies revealed the reaction to proceed through a singlet exciplex. The fluorescence of trans-1,2-bispyrazylethylene was quenched very efficiently by tetracyanoethylene with the quenching constant of $1.6 \times 10^{10} M^{-1} s^{-1}$ while electron rich olefin, tetramethylethylene, did not quench the fluorescence of bispyrazylethylene.

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. This elegant method has proved to be the efficient method to synthesize phenanthrenes and over 100 phenanthrenes have been synthesized by this method [1-10].
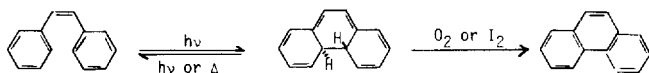

However, the method has some drawbacks depending on the substrates and conditions of hydrogen abstraction employed, of giving less or more low yields and forming by-products such as photooxides that are often difficult to separate.

When methylene chloride solutions of stilbenes, substituted stilbenes, and other 1,2-diaryl-substituted ethylenes in the presence of π-acceptors such as tetracyanoethylene, tetra-cyanoquinodimethane, chloranil, and bromanil were irradiated with the longest-wave absorption band of the stilbenes under anaerobic conditions, practically complete conversion of stilbenes to condensed polycyclic aromatic hydrocarbons was observed. [11]

trans-Bispyrazylethylene (*t*-BPE), a nitrogen containing stilbene analogue, has $^1(n, \pi^*)$ state which has about the same energy as $^1(\pi, \pi^*)$ state. Because of the (n, π^*) excited states, BPE shows quite different photochemical behavior from the ordinary stilbenes such as photoreduction [12] and photoaddition reactions to tetramethylethylene [13] through the $^1(n, \pi^*)$ state.

The synthesis of azaphenanthrenes by classical methods is very difficult. 1,4,5,8-Tetraazaphenanthrene, a new tetra-azaheteroaromatic compound, has been synthesized pho-tochemically in 90% yield from dilute benzene solutions of BPE in the presence of oxygen. Iodine was not suitable as the oxidant because it undergoes strong complexing with BPE and also enhances 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 reac-tive state for the cyclization in comparison to $^1(\pi, \pi^*)$ state for the ordinary stilbene derivatives. [14]
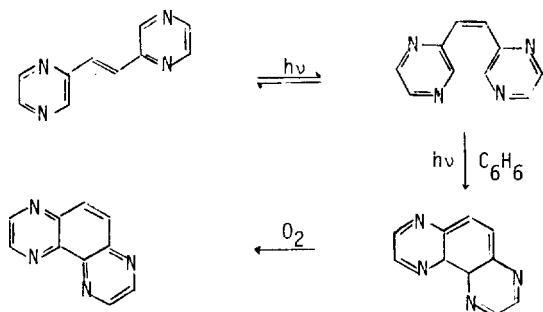
90%

Thus photolysis of BPE in the presence of a π-acceptor, tetracyanoethylene, is studied.

Experimental

Materials. *t*-BPE was synthesized from pyrazine carboxylic acid as reported. [15] Tetracyanoethylene (Merck) was sublimed, recrystallized from chlorobenzene, and sublimed again im-mediately prior to use. [16] All the solvents such as benzene, tetrahydrofuran, and acetonitrile were purified immediately prior to use by the known standard methods. [17]

Spectra. Nuclear magnetic resonance spectra were measured on a Varian T-60A spectrometer against tetramethylsilane in-ternal standard in acetone-d_6. 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 Hewlett Packard 5985 A mass spectrometer. Fluorescence spectra were recorded on a Aminco-Bowman spectrofluorometer with Aminco XY-recorder.

Photoreaction of t-BPE with Tetracyanoethylene. *t*-BPE (2.98 mM) and tetracyanoethylene (3.52 mM) were dissolved in benzene (200 ml) and irradiated in a preparative RPR 208 Rayonet reactor (The Southern New England Ultraviolet Company) equipped with 350 nm fluorescent lamps for 16 hr in a Pyrex vessel. The solution was stirred with a magnetic bar during the irradiation. The solution turned into deep green and trace amount of dark brown precipitate was formed. After filtration to remove the precipitate, about the half of the sol-vent was evaporated off with a rotary evaporator. The product was crystallized on the wall of the vessel on standing for 2 hr at room temperature. The precipitate was washed with cold benzene and dissolved in acetone.

Fluorescence Quenching of t-BPE by Tetracyanoethylene. The fluorescence intensity of *t*-BPE in benzene ($1.16 \times 10^{-4} M$) and in acetonitrile ($1.0 \times 10^{-4} M$) was monitored varying the concentration of tetracyanoethylene from $1.72 \times 10^{-4} M$ to $9.2 \times 10^{-2} M$.

Results and Disscussion

Product Analysis. The UV absorption spectra of the purified photoproduct in ethanol show a strong absorption at λ_{max} 267 nm and a weak band at λ_{max} 312 nm which are very similar to those of 2-methylpyrazine ($\lambda_{max}^{EtOH} 262$ (π, π^*), 306 nm (n, π^*)). Thus (π, π^*) band greatly blue shifted from 324 nm to 267 nm indicating the loss of the central double bond of *t*-BPE in conjugation. The infrared spectra neither show any olefinic stretching band near 1,640 cm^{-1} nor the out-of-plane C-H bending vibrations of *t*-BPE at 975 cm^{-1} substantiating the UV data. But the spectra show ν_{C-H} of pyrazine ring at 3,020-3,040 cm^{-1}, alkyl C-H stretching band at 2,920-2,960 cm^{-1}, $\nu_{C \equiv N}$ at 2,200 cm^{-1}, and 860 cm^{-1} band characteristic of cyclobutane ring implicating $2\pi + 2\pi$ C_4-photocycloaddition of *t*-BPE to tetracyanoethylene.
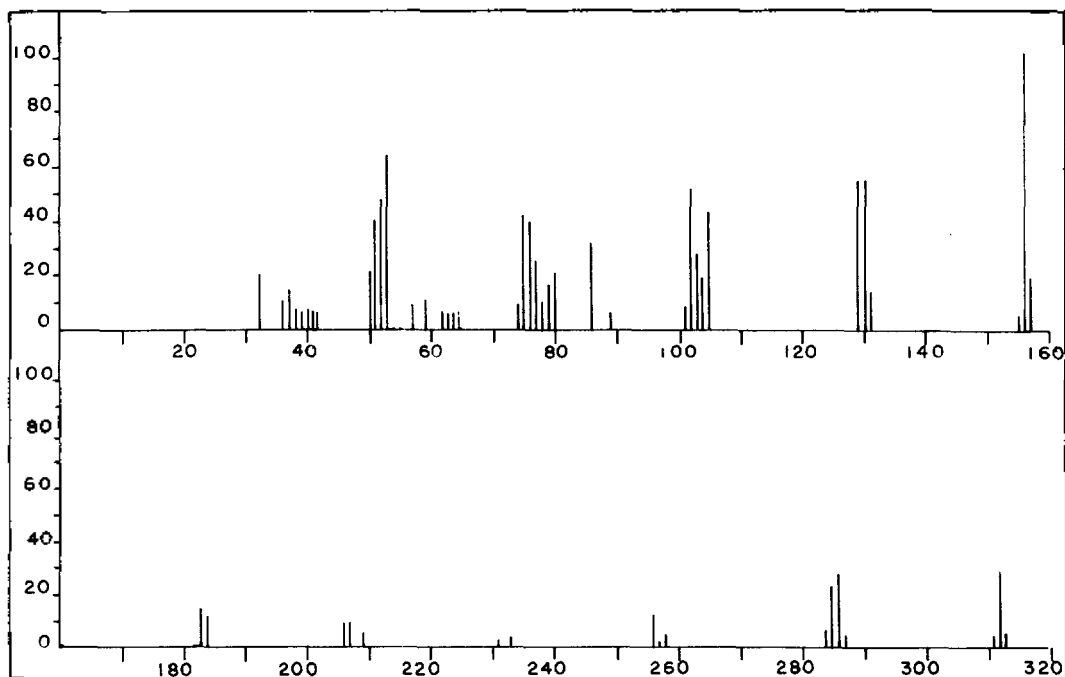
Figure 1. Mass spectrum of the photoproduct.

The NMR absorptions of the olefinic protons of t-BPE (δ7.83) and c-BPE (δ6.93) were absent supporting the cycloaddition at the double bond. The pyrzaine ring protons show a multiplet at δ8.81 (2H) and a singlet at δ9.00 (1H) and benzylic proton peak appears at δ5.77 (s, 1H). The spectra are consistent with the $2\pi + 2\pi$ C_4-cycloaddition structure.

The mass spectra (Figure 1) show the heaviest peak at m/e 312 which corresponds to the molecular ion peak of 1:1 t-BPE-tetracyanoethylene addition product. The base peak appears at m/e 156 which is exactly the half of the molecular weight of the adduct. This indicates that the compound easily undergo splitting on electron impact which is general in $2\pi + 2\pi$ C_4-cycloadducts.[18] The peak at m/e 184 corresponds to another cyclobutane ring cleaved product, BPE. The peaks at m/e 285 and 258 are due to M-HCN and M-2HCN respectively which are characteristic of the pyrazine ring fragmentation and the peak at m/e 286 is caused by the loss of CN group from the product. Thus all the spectral data are consistent with the structure of $2\pi + 2\pi$ C_4-cycloadduct between t-BPE and tetracyanoethylene.
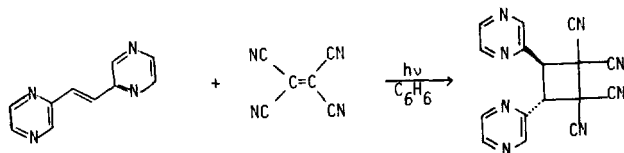
The compound is oxidized in a few seconds in the air and slowly oxidized in the solution which is not degassed. When four cyano groups are conjugated with the π-system like in tetracyanoethylene, the compound is reasonably stable but in tetracyanoethane, the σ-electrons of C-C single bond are strongly withdrawn by four cyano groups and the compound is readily

oxidized in the air.[19] This is in good agreement with the fact that the photoproduct is a 1:1 C_4-cycloadduct of t-BPE and tetracyanoethylene.

Fluorescence Studies and Reaction Mechanism. t-BPE is weakly fluorescent (Φ= 0.025 at 77°K) from $^1(\pi, \pi^*)$ compared to the strong fluorescence of *trans*- stilbene (Φ= 1.0 at 77°K). The fluorescence of t-BPE was efficiently quenched by tetracyanoethylene in acetonitrile with a k_q of $1.6 \times 10^{10} M^{-1} s^{-1}$ which is close to diffusion controlled rate constant. In benzene, k_q was $4.4 \times 10^{11} M^{-1} s^{-1}$ which is bigger than k_{diff}. This is due to the trivial singlet energy transfer from the excited singlet BPE to ground state benzene-tetracyanoethylene charge-transfer complex which has strong absorption with λ_{max} at 382 nm and the absorption spectra of the C-T complex overlap extensively with the fluorescence spectra of t-BPE. Consequently the much of the fluorescence of t-BPE is absorbed by the C-T complex and k_q is anomalously large.

Thus the $2\pi + 2\pi$ photocycloaddition of t-BPE to tetracyanoethylene seems to proceed through a singlet excited state of t-BPE, possibly through a singlet exciplex between excited t-BPE and ground state tetracyanoethylene. When t-BPE is irradiated with benzophenone, only *cis*$\rightleftharpoons$*trans* isomerization of t-BPE is observed and no cycloaddition is apparent.

Irradiation of either *trans*- or *cis*-stilbene in tetramethylethylene, and electron rich olefin, gives a $2\pi + 2\pi$ C_4-photocycloadduct in high yields.[20] The mechanism of this photocycloaddition involves reversible reaction of $^1(\pi, \pi^*)$ *trans*-stilbene with ground state tetramethylethylene giving an exciplex which demotes to the adduct with retention of the *trans*-stereochemistry. The same mechanism seems to work for the photoaddition of t-BPE to tetracyanoethylene. The fluorescence of t-BPE is not quenched by tetramethylethylene

because of the short lifetime of $^1(\pi, \pi^*)$ state of BPE and no exciplex is formed between BPE and tetramethylethylene and noncyclic photoaddition product is obtained when BPE is irradiated in tetramethylethylene through an allylic hydrogen atom abtraction of tetramethylethylene by $^1(n, \pi^*)$ state of BPE.[13]

Because of four nitrogen atoms in pyrazine rings of BPE, no ground state charge transfer complex is formed between *t*-BPE and tetracyanoethylene in contrast to stilbene and tetracyanoethylene case. Thus, stilbene undergoes photodehydrocyclization to phenanthrene when irradiated with tetracyanoethylene but BPE froms a singlet exciplex which leads to a $2\pi + 2\pi$ C_4-photocycloadduct on irradiation with tetracyanoethylene in acetonitrile.

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Synthesis of N⁶-Aminoalkyl-5'-adenylic Acid Derivatives

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Seventeen new N⁶-aminoalkyl derivatives of 5'-adenylic acid and adenosine 5'-triphosphate (Compound I-XVII) were synthesized from 6-chloropurine ribonucleoside by reaction with appropriate diamines. This paper discusses the procedure of synthesis and the identification of the derivatives by ultraviolet spectra, high voltage electrophoresis, paper chromatography, elemental analyses, and other chemical methods.

Introduction

Both of the 5'-adenylic acid (adenosine 5'-monophosphate, AMP) and adenosine 5'-triphosphate (ATP) which is a carrier of phosphate and pyrophosphate in several important enzymatic reactions involved in the transfer of chemical energy, are substrate of a large portion of known enzymes and are utilized frequently in metabolism as allosteric regulators of enzyme activity.[1,2] Most analogs of adenosine used in the neoplastic chemotherapeutic agents may react with the enzyme of adenylic pyrophosphorylase, whereas hypoxanthine and guanine analogs are substrates for the enzyme inosinic-guanylic pyrophosphorylase.[3] Antimetabolites, as the anticancer agents, are structural analogs of physiologically occurring substances which can produce evidence of deficiency of the metabolites in a biological system.[4] Since the pioneering studies of Hitchings and his associates, a large number of