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The Photocycloaddition of 6-Substituted Phenanthridines to Electron-rich Olefins

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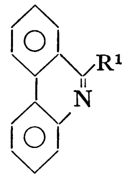
The photocycloaddition reaction of 6-substituted phenanthridines and electron-rich olefins, such as *trans*-anethole and phenyl vinyl ether, is described. This reaction proceeds from the $^{1}(\pi,\pi^{*})$ states of 6-substituted phenanthridines *via* the exciplex to give azocine and/or azetidine derivatives in ethanol.

Photocycloaddition between multiple bonds seems to be common and many papers have been reported in this area.1) However, the intermolecular photocycloaddition reactions of the carbon-nitrogen double bond are documented only for the cyclic imines, which are classified into two groups. One of them is the system where the carbon-nitrogen double bond is conjugated with the imino2) or the carbonyl group,3,4) while the other one is the system where a hetero atom, such as nitrogen,4) oxygen,5) and sulfur,6) is attached to the imino linkage.

Our concern has been concentrated on the photochemical behavior of phenanthridine, and we have already reported its luminescence phenomena and photoesterification reaction.7) Phenanthridine(**1**), which is isoelectronic to phenanthrene, can also be expected to undergo photocycloaddition reactions with olefins similar to phenanthrene derivatives.8) We have probed the photochemical reactivity of **1** with olefins and wish now to present some novel photocycloaddition reactions of **1** with electron-rich olefins(**2a**—**c**).9)



1a: $R^1=CH_3$
1b: $R^1=CN$

Experimental

Materials. **1a** and **1b** were synthesized according to the literature.10 11) **1a**: mp 78.4—79.0 °C; NMR (δ) 7.46—8.51 (m, 8H), 2.94 (s, 3H); IR (cm^{-1}) 1615, 751, 720; UV (EtOH, nm) 254.5 (ε=36000), 329.6 (ε=3900), 344.5 (ε=3900). **1b**: mp 136—137 °C; NMR (δ) 7.57—8.82 (m, 8H); IR (cm^{-1}) 2220, 1608, 758, 722; UV (EtOH, nm) 257.0 (ε=28000), 351.2 (ε=2500), 367.9 (ε=2200).

Benzene was purified by the conventional method and was finally distilled. The following solvent and quenchers (reagent special grade) were used without further purification: ethanol, *N,N*-dimethylaniline, *trans*-anethole (**2a**), pyrrole, 1-methyl-pyrrole, triethylamine, β-methylstyrene, quinoline, 2,3-dimethyl-2-butene, furan, γ-picoline, *trans*-1,3-pentadiene, acrylonitrile, and pyridine.

The benzophenone and benzhydrol were recrystallized from hexane-benzene and ethanol respectively; benzophenone, mp 48.5—48.7 °C, benzhydrol, mp 68.9—69.2 °C.

cis-Anethole (**2b**) was prepared by Michler's ketone (10^{-2} M†)-sensitized isomerization of **2a** (10^{-1} M). The subsequent separation of **2b** from **2a** by column chromatography (silica gel, hexane) gave pure **2b** in a 50% yield. **2b**: colorless oil; NMR (δ) 1.86 (dd, 3H), 3.74 (s, 3H), 5.80 (m, 1H), 6.38 (dd, 1H), 6.82 (d, 2H), 7.25 (d, 2H); IR (cm^{-1}) 2870, 1609, 1510, 1250, 1178, 1038, 845.

Phenyl vinyl ether was synthesized according to the literature.12) Its IR and NMR spectra were superimposable on those of an authentic sample.

Instrumental. The GC analyses were done on a Shimadzu GC-6A-FID apparatus equipped with a column of 5% OV 17 on chromosorb p. The products were analyzed on a Waters liquid chromatograph, Model 440, equipped with a column of μ-PORASIL. Photocycloadducts were also isolated by HPLC. The IR spectra were taken either on a JASCO Model IR-G Spectrophotometer or on a Shimadzu IR-420 Infrared Spectrophotometer. The NMR spectra were obtained either on a JEOL JNM-PMX (60 MHz) or on a Varian EM 360A NMR Spectrometer (60 MHz), using Me_4Si as the internal standard. The UV spectra were recorded on a JASCO NEW-UV-210A Digital Double-beam Spectrophotometer. The fluorescence and phosphorescence spectra were taken either on a Hitachi MPF 4A or on a Shimadzu RF-502A Fluorescence Spectrophotometer. The melting points were measured by means of a Yazawa Hot Plate and are uncorrected.

Irradiations. Irradiations on a preparative scale were carried out with Pyrex-filtered light from a 400-W high-pressure mercury lamp (Riko) under the continuous bubbling of nitrogen in an immersion apparatus at the temperature of running water. The samples for kinetic studies and the controlled experiments were irradiated using a merry-go-round mounted on an optical bench. The light source was a 200-W super-high-pressure mercury arc, and light at 366 nm was selected through a Shimadzu-Bausch-Lomb monochromator.

Irradiations of 1 and 2. **1** (10^{-2} M) was irradiated in benzene or ethanol (200 ml) in the presence of **2** (10^{-1} M). The reaction mixtures were separated by means of column chromatography (Florisil, hexane–ether), and the products were purified by preparative HPLC. The products were identified by means of IR and NMR.

Quenching of the Photocycloaddition Reaction of 1 to 2. A 10 ml ethanol solution of **1** (10^{-2} M) with **2** (10^{-1} M) was irradiated in the absence or presence of a quencher, such as acrylonitrile and *trans*-1,3-pentadiene (10^{-1} M). The reactions were then monitored by means of HPLC.

Quantum Yield for the Formation of 3ba. Benzophenone-benzhydrol actinometry was used ($\lambda_{\text{irrad.}}$=366 nm).13) The reactions were monitored by means of HPLC.

Results and Discussion

*Quenching of **1a** Fluorescence.* **1a** fluoresces only in hydroxyl solvents, such as ethanol and benzene-acetic acid.7)

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† 1 M=1 mol dm^{-3}.

Figure 1 shows that the **1a** fluorescence is attenuated by **2a** in ethanol, accompanied by the growing-in of a new emission at a longer wavelength. The **1a** fluorescence is also quenched by other electron-rich olefins and amines at almost the diffusion-controlled rate, and a new emission is observed similarly in the cases of triethylamine, pyrrole, 1-methylpyrrole, β-methylstyrene, and 2,3-dimethyl-2-butene. Figure 2 shows the correlation of the log k_q for **1a** with the ionization potential of the quencher(IP_Q).

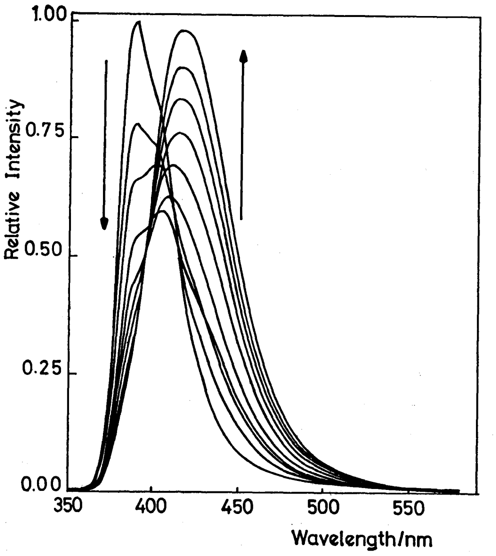


Fig. 1. Quenching of **1a** fluorescence by **2a** in ethanol at room temperature: concentration of **1a**$=1.60\times10^{-2}$ M, excitation wavelength=353.1 nm, $K_{SV}=18.1$ M^{-1}.

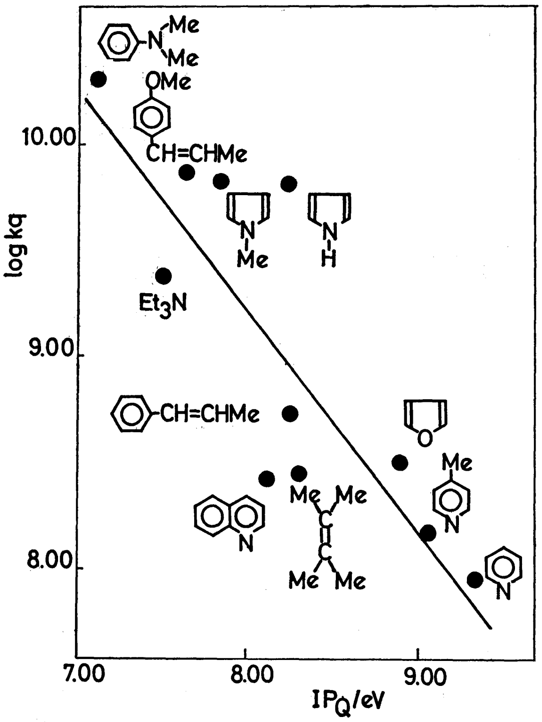
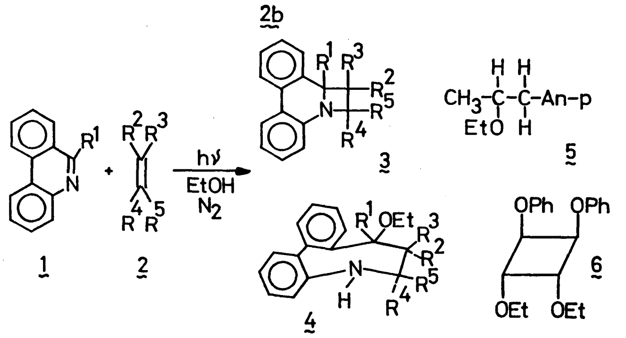


Fig. 2. Correlation of log k_q for **1a** with IP_Q; in EtOH under air, at room temperature.

The new emission is indicative of exciplex formation, and the good correlation of log k_q with IP_Q suggests that charge-transfer interaction is dominant in the above systems. Although it is generally accepted that exciplexes dissociate into radical ion pairs in a polar solvent and that exciplex emission is weak, in these cases a fairly strong exciplex emission is observed, even in a polar hydroxyl solvent.

*Photocycloaddition of **1a** with **2a** in Ethanol.* The azocine derivative **4aa** was afforded in a 56% yield, instead of the expected azetidine derivative, **3aa**. It is noteworthy that **5** was obtained in a 40% yield. **5** probably arises from the radical cation $\mathbf{2a}^{+\cdot}$ *via* the *anti*-Markownikov addition of ethanol. This fact indirectly supports the exciplex formation, followed by its dissociation into radical ions.[14] In changing the solvent from ethanol to methanol or 2-propanol, the corresponding *anti*-Markownikov adducts were obtained. The yields were in the order of: methanol≅ethanol≧2-propanol. Although only 30% of the isomerization from **2a** to **2b** occurs on the direct irradiation of **2a**, 74% of the recovered anethole is *cis* in this reaction. It is known that exciplex formation often enhances intersystem crossing;[15] the observed fact suggests the presence of such a path for the collapse of the exciplex, which leads to the photoiso-



1a: $R^1=CH_3$
1b: $R^1=CN$
2a: $R^2=p$-Methoxyphenyl, $R^3=R^4=H$, $R^5=CH_3$
2b: $R^2=p$-Methoxyphenyl, $R^3=H$, $R^4=CH_3$, $R^5=H$
2c: $R^2=PhO$, $R^3=R^4=R^5=H$

Scheme 1. Photochemical reactions of **1** with **2** in ethanol.

Table 1. Photocycloaddition reactions of 1 with 2 in ethanol

Substrate	Olefin	Irradiation time/h	Products (yield/%)
1a	**2a**	29	**2b** (37) **4aa** (56) **5** (40)
1a	**2b**	30	
1b	**2a**	5	**2b** (47) **3ba** (16) **4ba** (84)
1b	**2b**	6	
1b	**2c**	26	**4bc** (42) **6** (5)

merization from **2a** to **2b**.[16,17]

*Photocycloaddition of **1b** with **2a** in Ethanol.* **1b** reacted much faster than **1a** to give **3ba** and **4ba** in 16 and 84% yields respectively. The formation of both **3ba** and **4ba** greatly intrigued us as to the reaction course by which **4** is formed. In this reaction, 52% of the anethole was **2b**. However, no **5** was obtained.

*Photocycloaddition of **1** with **2b** in Ethanol.* As has been described above, no incorporation of **2b** into the photocycloadducts was observed, though a considerable amount of **2b** was accumulated after the photocycloaddition reaction of **1a** or **1b** with **2a**. Thus, **1a** or **1b** was irradiated in the presence of **2b**, but no photocycloadduct was obtained in either case. The unreactive nature of **2b** toward the excited state of **1** is ascribable to the following facts. (1) The non-emissive (**1**–**2b**) exciplex collapses to the ground states much faster than the (**1**–**2a**) exciplex, partly because of its instability caused by its less efficient resonance stabilization between the two molecules, and (2) the exciplex substitution might be occurring, as in the case of (9-cyanophenanthrene–**2b**) exciplex.[18] The quenching rate of S_1 of **1b** by **2b** ($k_q=6.6\times10^9\ M^{-1}\ s^{-1}$) is slower than the quenching by **2a** ($k_q=1.7\times10^{10}\ M^{-1}\ s^{-1}$), and the $(\mathbf{1b}\text{–}\mathbf{2b})^*+\mathbf{2a}\rightarrow(\mathbf{1b}\text{–}\mathbf{2a})^*+\mathbf{2b}$ reaction would be exothermic.

*Photocycloaddition of **1b** with **2c** in Ethanol.* **1b** was irradiated in the presence of **2c** to give **4bc** and **6** in 42 and 5% yields respectively. It has been reported that the radical cation of **2c** reacts with **2c** to give cyclobutane dimers,[19] but in our study no such compounds were obtained.

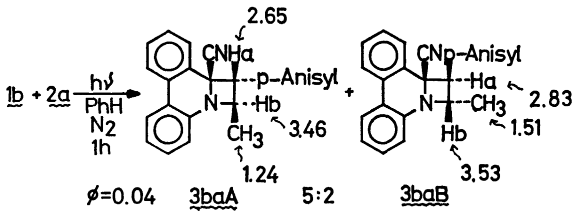
Table 2 summarizes the spectroscopic data of the products.

*Photocycloaddition of **1a** with **2a** in Benzene.* Even on the prolonged irradiation of **1a** and **2a** in benzene (99 h), no **3** was afforded, and **1** was recovered quantitatively, but a **2a** dimer[20] and **2b** were obtained in 49 and 32% yields respectively. These facts indicate that no photocycloaddition reaction between excited **1a** and **2a** proceeded.

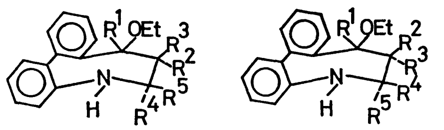
*Photocycloaddition of **1b** with **2a** in Benzene.* A stereoisomeric mixture of **3** was obtained in a 52% yield on the irradiation of **1b** with **2a** in benzene for 1 h. The quantum yield for the formation of **3ba** was 0.04. This value is around a tenth as large as that for the formation of the cycloadduct between 9-cyanophenanthrene and **2a**.[18]

***3** as Precursor for **4**.* The irradiation of **3** in ethanol for 1 h gave **4** in a 50% yield, and its original stereochemistry was retained. This fact shows that **3** is the precursor for the formation of **4**.

Exciplex as Intermediate. Exciplexes have been postulated as intermediates in the photocycloaddition reactions of phenanthrene[21–23] or 9-cyanophenanthrene[18,24] by simultaneous observations of exciplex emission and photocycloadduct formation. Recently,

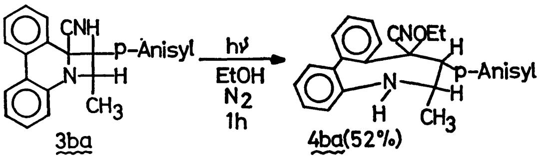


Scheme 3. Photocycloaddition reaction of **1b** with **2a** in benzene.



4A 4B

Scheme 2. Stereoisomers of **4**.



Scheme 4. Intermediacy of **3**.

TABLE 2. SPECTROSCOPIC DATA OF THE PRODUCTS

Compd	NMR δ								IR ν/cm⁻¹
	R^1	R^2	R^3	R^4	R^5	CH_3CH_2O	N-H	Aromatic H	
4aaA	1.29(s)	3.76(s) (CH_3O)	3.02(d)	2.02(dq)	1.21(d)	3.68(q) 1.28(t)	3.42(s)	6.50—8.57(m)	3350(N-H) 1176(C-O)
4baA		3.62(s) (CH_3O)	3.78(d)	3.37(dq)	1.21(d)	3.70(q) 1.05(t)	3.70(s)	7.10—8.59(m)	3340(N-H) 2250(C≡N)
4baB		3.62(s) (CH_3O)	3.81(d)	3.41(dq)	1.23(d)	3.70(q) 1.05(t)	3.70(s)	7.10—8.59(m)	3340(N-H) 2250(C≡N)
4bcA			5.12(dd)	4.47(d)	4.62(d)	3.36(q) 0.95(t)	3.39(s)	6.50—8.47(m)	3320(N-H) 2250(C≡N)
4bcB			5.24(dd)	4.17(d)	4.04(d)	3.36(q) 0.95(t)	3.39(s)	6.50—8.47(m)	3320(N-H) 2250(C≡N)
5	1.07(d, 3H), 1.08(t, 3H), 2.55(d, 1H), 2.67(d, 1H), 3.37(q, 2H), 3.39(dd, 1H), 3.69(s, 3H), 6.69(d, 2H), 7.00(d, 2H)								1175(C-O)
6	1.17(t, 6H), 3.50(q, 4H), 3.69(d, 2H), 3.97(d, 2H), 6.90—7.46(m, 10H)								1249(C-O) 1124(C-O)

Caldwell *et al.* have, by a kinetic study together with the spectroscopic evidence, established the exciplex as the intermediate in the photocycloaddition reaction of 9-cyanophenanthrene to **2a**.[18]

The (**1b**–**2a**) exciplex emission was quenched by acrylonitrile, which did not attenuate the **1b*** fluorescence. Acrylonitrile (10^{-1} M) also quenched the product formation in the photocycloaddition reaction of **1b** and **2a**, while the triplet quencher, *trans*-1,3-pentadiene did not suppress the formation of the photocycloadducts. These facts indicate that the singlet exciplex is the intermediate in this photocycloaddition reaction.

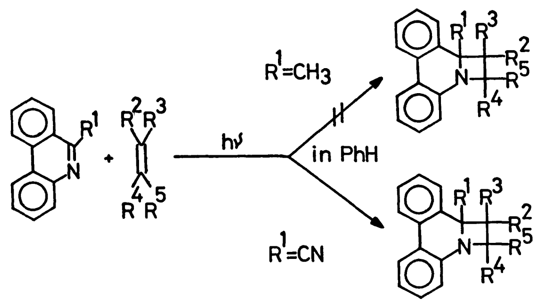
*Stereochemistry of **3** and **4**.* LC analysis and NMR spectroscopy revealed that this photocycloaddition reaction proceeds regiospecifically, but that stereospecificity is low. **4b** was given as a mixture of the stereoisomers. The molar ratio of **A** to **B** is 4:3 in **4ba** and 8:5 in **4bc**. The less sterically hindered **A** predominated over **B**, and the above ratio reflects the ratio of **3**, which is the precursor of **4**. In fact, **3ba** was obtained as a mixture of the stereoisomers in a 5:2 (**3baA**: **3baB**) ratio in benzene. As Scheme 3 shows, the Hb proton of **3baA** appeared at a higher field than that of **3baB**. This is due to the diamagnetic anisotropy of the cyano group, which is *trans* to the Hb proton.[18b] The stereochemical assignment of **4** was based on the fact that the methyl protons(R^5) of the cycloadduct absorb at a magnetic field lower than 1 ppm.[25] This fact indicates that the methyl group (R^5) is *trans* to the aromatic ring.

The reason for the low stereospecificity even *via* the exciplex intermediate is not yet certain. We presume that the oriented structures of the exciplexes in these cases are not bound tightly; also the exciplexes may have two different structural orientations. The lack of any incorporation of **2b** into **3** or **4** suggests that the photodimerization from **2a** to **2b** competes with the photocycloaddition of **1** to **2a** and that the collapse of the exciplex to a biradical which gives a random stereoisomeric mixture of the adducts is unfavorable.

Solvent Effect. As Scheme 5 shows, a clear solvent effect is observed in this reaction. This may be ascribed to the different nature of the S_1 of **1** depending on the solvent. Table 3 clearly shows that the photocycloaddition reaction is governed by the nature of the S_1 of **1**. In ethanol, the emissive S_1 of **1** is of (π,π^*) and can undergo photocycloaddition with **2**. In benzene, the S_1 of **1a** is non-emissive, and its lifetime is considered to be shorter than in ethanol. The unreactive nature of **1a** in benzene may be ascribable to the (n,π^*) character of the S_1 of **1a**, whose short lifetime may be anticipated to be attributable to its non-emissiveness. That would be why **1a** is unreactive toward **2** in benzene. On the other hand, the S_1 of **1b** is of (π,π^*) even in benzene.[7] The simultaneous fluorescence emission and cycloadduct formation in this case support the above explanation.

Scheme 6 shows a plausible reaction scheme of the observed reaction.

In conclusion, we have found the novel photocycloaddition reaction of **1** with **2a** and **2c**. This reaction proceeds from the $^1(\pi,\pi^*)$ state of **1** to give **4** *via* **3**. The exciplex is considered to be the intermediate of **3**. The above reaction is affected by the solvent and by the structure of olefin.

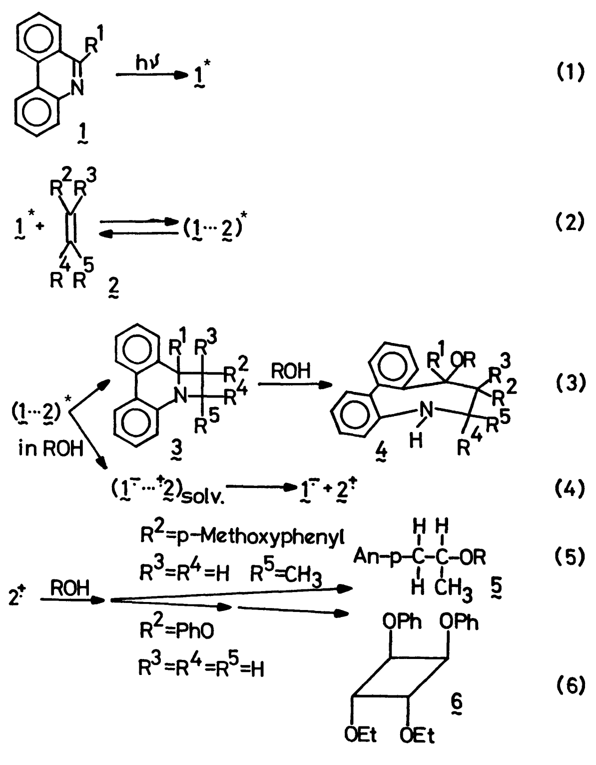


$R^2 = p$-Methoxyphenyl, $R^3 = R^4 = H$, $R^5 = CH_3$

Scheme 5. Solvent effect on photocycloaddition of **1** with **2a**.

Table 3. Solvent effect on the fluorescent state of **1**

	Fluorescence λ_{max}/nm	Excited state	Photocycloaddition
Benzene			
1a	Not observed	$^1(n,\pi^*)$	No
1b	401	$^1(\pi,\pi^*)$	Yes
Ethanol			
1a	388	$^1(\pi,\pi^*)$	Yes
1b	410	$^1(\pi,\pi^*)$	Yes



Scheme 6. Plausible reaction scheme.

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