pH-Dependency of Photocyclization of Diarylfumaronitriles

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The photocyclization of diarylfumaronitriles in aqueous ethanol is influenced by pH. The product ratio of 9,10-dihydro-9,10-dicyanophenanthrenes (IV) decreases with decrease in pH. Discussion is given on the acid-catalyzed isomerization of the 4a,4b-dihydrophenanthrenes to IV from results of observation of the colored intermediate.

Some stilbenes substituted by electron-withdrawing groups at the olefinic double bond give 9,10-dihydrophenanthrenes along with the phenanthrenes on UV irradiation,[1] while stilbene yields only phenanthrene but no 9,10-dihydro derivative as a photoproduct.[2-5] The product ratio of the 9,10-dihydrophenanthrenes to the phenanthrenes in the former case depends on the reaction conditions.[1] We confirmed that the yield of 9,10-dicyanophenanthrene (IIIa) undergoes a solvent effect when diphenylfumaronitrile (Ia) is irradiated in solution (Table 1). 9,10-Dihydro-9,10-dicyanophenanthrene (IVa) is formed almost exclusively in acetic acid. This indicates that the formation of dihydro derivative (IVa) is influenced specifically by the acidic nature of the solvent. This was confirmed by the sole production of IVa when Ia was irradiated in ethanol containing a trace of sulfuric acid. These observations led us to investigate the pH-dependency of the photoproduct distribution. In this paper we report the pH-dependency of several diarylfumaro- and maleonitriles (I and II) and propose a cyclization mechanism *via* 4a,4b-dihydrophenanthrenes,[6] in contrast to the free-radical mechanism proposed recently by Srinivasan and Hsu.[7]

Results

Since diarylfumaronitriles (I) are practically insoluble in water, buffered aqueous ethanol (50 w/w%) was employed as a solvent. Although all the UV absorption spectra of Ia at pH less than *ca.* 10 were identical and remained unchanged on standing in the dark, the absorbance at the longest wavelength in more alkaline solutions (*ca.* 0.1 M NaOH) decreased gradually on standing at room temperature. The electron-withdrawing group at the phenyl ring of the fumaronitrile makes the double bond so sensitive toward the alkaline medium that the absorption bands at the greatest wavelength of α-(*p*-chloro- and cyanophenyl)-α'-phenylfumaronitriles (Ib and Ic) disappear gradually even at pH *ca.* 8. The decrease of the absorbance may occur as a result of the alkali catalyzed hydration on the olefinic double bond of the fumaronitrile, as in the case of α-arylcinnamonitrile.[8] We have employed buffered solutions ($pH<8$) for studies on the pH-dependency of the photolysis.

In order to obtain some information on the pH effect on the photolysis of diarylfumaronitrile, aerated solutions at various pH were irradiated with light of 330 nm, and the UV spectra were recorded at intervals. Typical examples for Ia are illustrated in Fig. 1. A family of the absorption curves changed at various pH; 9,10-dihydro-9,10-dicyanophenanthrene (IVa) forms predominantly in a weakly acidic solution whereas the formation of 9,10-dicyanophenanthrene (IIIa) is observed in neutral or alkaline solutions.

It has been emphasized that diagrams of quotients of extinction differences (EDQ diagrams) can be utilized to distinguish complicated photoreactions followed UV-spectroscopically.[9] Examination of the EDQ diagrams for Ia at various pH revealed that the elementary reactions depend also on the pH of the solution; both EDQ diagrams at pH 7.0 and 5.0 are linear but that at pH 9.0 is non-linear (Fig. 1). It is therefore concluded that two elementary reactions take part in the photoreaction of Ia at pH 7.0 and 5.0, while more complex reactions occur at pH 9.0. The photolysis of the fumaronitrile (Ia) at pH less than *ca.* 7.0 thus consists of the initial photoisomerization to the maleonitrile (IIa) and the photoinduced transformation of IIa to the phenanthrenes (IIIa+IVa).[10] Similar results were obtained when α-(*p*-methoxyphenyl)-α'-phenylfumaronitrile (Id) was used. The EDQ diagram of the photoreaction of α-(*p*-cyanophenyl)-α'-phenylfumaronitrile (Ic) was found to be non-linear even at pH 7.0, while a linear EDQ diagram was obtained when the photolysis was carried out at pH 4.0.

Table 1. Solvent effect on the yield of 9,10-dicyanophenanthrene

Solv.	Yield of 9,10-dicyano-phenanthrene (%)
Cyclohexane	80
Chloroform	10—20
Toluene	70
EtOH	30
AcOH	Trace[a]
EtOH-H_2SO_4	0[b]

a) The remaining product is 9,10-dihydro-9,10-dicyanophenanthrene. b) The 9,10-dihydro compound forms exclusively.

The pH-dependency of the photocyclized product distribution was determined by the UV spectra of the photolyzed solutions at various pH where linear EDQ diagrams were obtained. The results for Ia are given in Table 2. The UV spectra of the solutions irradiated at pH less than 4 are identical with that of the dihydro compound (IVa). A family of the absorption curves for Ia intersect at 265 and 295 nm. The peaks at 326 and 339 nm due to the phenanthrene (IIIa) increase with increase in the pH of the solutions at the same ratio. It is concluded that only IIIa and IVa are concerned in the product distribution. The product distribution from diphenylmaleonitrile was found to be practically identical with that from the fumaronitrile (Fig. 3). The absorption spectra of the irradiated solutions in alkaline medium deviated from the isosbestic points at 265 and 295 nm. This is in line with the anomalous photochemical behavior of this compound in alkaline region as revealed by an examination of the EDQ diagram. The other *p*-substituted diphenylfumaronitriles undergo a similar pH effect on the product distribution. The yields of the 9,10-dicyanophenanthrenes (III) at various pH were estimated by the absorbance at the longest wavelength and plotted against pH as shown in Fig. 3. The yield of phenanthrene at a given pH value increases with an increase in the electron-withdrawing power of the substituent.

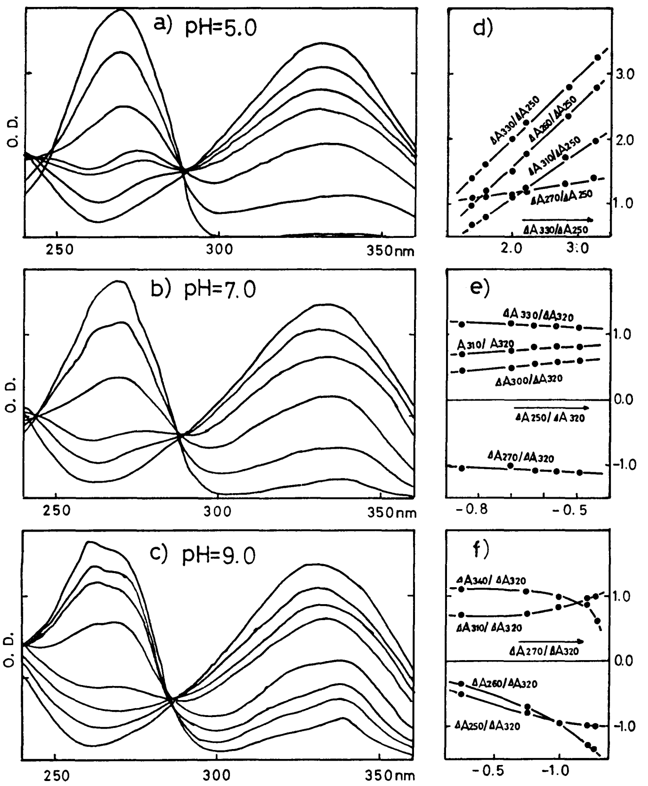


Fig. 1. The electronic absorption spectra recorded at intervals for the UV irradiation of diphenylfumaronitrile in aq. ethanol at various pH ((a): pH=5.0, (b): pH=7.0, and (c): pH=9.0) and the corresponding EDQ diagrams ((d): pH=5.0, (e): pH=7.0, and (f): pH=9.0).

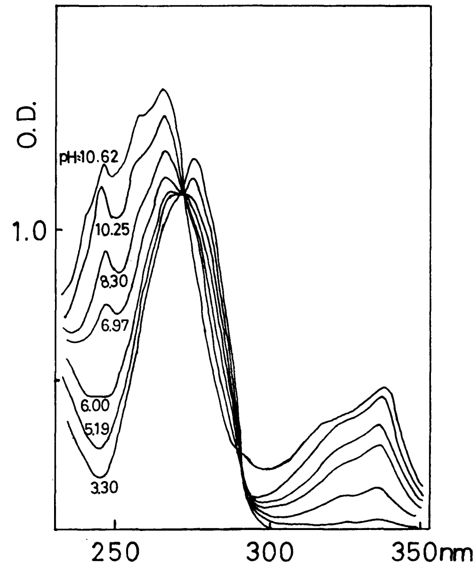


Fig. 2. The electronic absorption spectra of photoproducts from diphenylfumaronitrile irradiated in aq. ethanol at various pH.

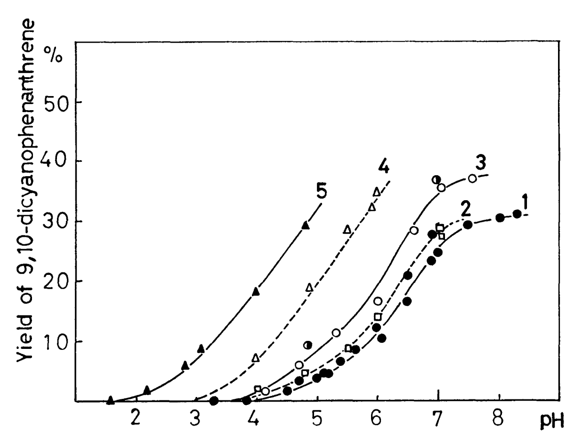
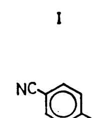


Fig. 3. pH-Dependency of the yield of 9,10-dicyanophenanthrenes; (1) 9,10-dicyanophenanthrene at 20 °C (—●—), (2) 3-methoxy-9,10-dicyanophenanthrene at 2 °C(--□--), (3) 9,10-dicyanophenanthrene at 2 °C (—○— from the fumaronitrile, —◐— from the maleonitrile), (4) 3-chloro-9,10-dicyanophenanthrene at 2 °C (--△--), (5) 3,9,10-tricyanophenanthrene at 2 °C (—▲—).

As regards the effect of nitrile groups on the pH-dependency, two isomeric stilbenes, α-phenyl-β-(*p*-cyanophenyl)acrylonitrile (V) and *p*,*p*′-dicyanostilbene (VI), were irradiated in acidic solutions. The former underwent a pH effect similar to that of Ia, giving no 3,9-dicyanophenanthrene in acidic solutions of pH less than *ca.* 4. However, the photoreaction of the latter was not affected by the pH. The photocyclization of stilbene itself in ethanol was not influenced by addition of sulfuric acid.

We found that red coloration (λ_{max}=480 nm in toluene) occurs at room temperature on the excitation of Ia with 330 nm light in some solvents such as aromatic hydrocarbons and chloroalkanes. Although there was



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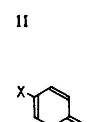

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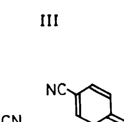

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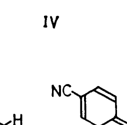
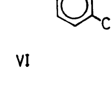
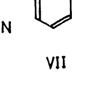


IV

V

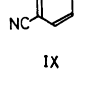


VI



VII

VIII



IX

no observation of such coloration in ethanol at room temperature, the solution of Ia was found to be faintly colored at −77 °C. Bleaching of the red color was accelerated by irradiation with visible light (*ca.* 480 nm), but retarded by the lowering in temperature. The bleaching corresponds to the first order decay with a half lifetime of 100 s in toluene at room temperature.

Discussion

Stilbene photocyclizes to phenanthrene through unstable yellow colored 4a,4b-dihydrophenanthrene.[2-5,11] Sargent and Timmons have suggested that the photocyclization mechanism for Ia is similar to that of stilbene, although no experimental evidence has been presented.[1] During the course of our investigation, Srinivasan and Hsu proposed an alternative free-radical chain mechanism for this type of photocyclization.[7] They observed the incorporation of deuterium from deuterated solvents into 9,10-dihydro compounds and the dependency of quantum yield on light intensity, and concluded that the abstraction of solvent hydrogen by the excited stilbene initiates the free-radical chain reaction to afford the 9,10-dihydrophenanthrenes. The mechanism can not fully explain the pH effect of the present work.

Our observation of the transient coloration on irradiation of Ia suggests the formation of 4a,4b-dihydro-9,10-dicyanophenanthrene (VIIa) as the intermediate like that in the case of stilbene.[5] The failure to observe the intermediate (VIIa) in aqueous ethanol UV-spectroscopically may be due to the shorter half life-time. The pH-dependency of the product distribution is thus explained by the acid catalyzed isomerization of the short-lived 4a,4b-dihydrophenanthrene (VII) to the 9,10-dihydro derivative (IV) as follows: The intermediate could be protonated at the cyano group to aromatize one of the ring, followed by the further migration of proton to give IV. The exclusive formation of the 9,10-dihydrophenanthrene on irradiation of α-phenyl-β-(*p*-cyanophenyl)acrylonitrile (V) in acidic solution seems to be in line with the reaction pathway. Protonation on the cyano group at the 9-position of the 4a,4b-dihydro compound (VIII) may promote the formation of the corresponding 9,10-dihydro compound in the same way. The insensibility of the photocyclization of isomeric *p*,*p*′-dicyanostilbene (VI) toward acid is in line with the processes; the proton catalyzed isomerization of the 4a,4b-dihydro (IX) to the 9,10-dihydro derivative can hardly occur since proton catalyzed aromatization is unfavorable in this case.

TABLE 2. THE KINETIC PARAMETERS (see Eq. 3).

X	Temp (°C)	log (k_3/k_1)	k_2/k_1
H	20	6.5	2.8
H	2	6.0	2.4
OMe	2	6.2	2.6
Cl	2	5.2	2.3[a)]
CN	2	4.2	1.7[a)]

a) The values were estimated so that a straight line with a gradient −1 was obtained according to Eq. 3.

The following kinetic aspects confirm the cyclization mechanism *via* VII. As shown in Fig. 1, the 9,10-dihydrocompounds (IV) are formed even in neutral or alkaline solutions, the yield being scarcely influenced by pH at pH 7—8 (Fig. 3). The results indicate that hydroxide ion plays a minor catalytic role in the process giving the photoproducts, and that the isomerization of VII to IV involves also the process irrespective of acid.

$$\begin{tikzcd} & & & \text{III} \\ \text{I} \arrow[r, shift left] & \text{II} \arrow[l, shift left] \arrow[r, shift left] & \text{VII} \arrow[l, shift left] \arrow[ur, "a)"] \arrow[dr, "b)"] \arrow[dr, shift right=2, "c)\ H^+"'] & \\ & & & \text{IV} \end{tikzcd} \qquad (1)$$

The reaction of the intermediate (VII) to give products thus consists of the following three paths as illustrated in Eq. 1 : *a*) oxidative formation of III, *b*) spontaneous isomerization to IV, and *c*) acid catalyzed isomerization to IV. We thus obtain the following equation in the region pH< 7.:

$$[\mathrm{D}]/[\mathrm{P}] = k_2/k_1 + k_3/k_1\cdot[\mathrm{H}^+] \qquad (2)$$

and then

$$\log([\mathrm{D}]/[\mathrm{P}] - k_2/k_1) = \log(k_3/k_1) - \mathrm{pH} \qquad (3)$$

where [D] and [P] are the yields of IV and III, respectively, k_1, k_2, and k_3 corresponding to the rate constant of paths *a*, *b*, and *c*, respectively. According to Eq. 2, the ratio of the rate constants k_2/k_1 is assumed to be [D]/[P] at pH=7. The plot log ([D]/[P]−k_2/k_1) against pH gives a straight line with a gradient −1 in agreement with Eq. 3 when the estimated values for k_2/k_1 were used in the cases of Ia and Id (Fig. 4). Since the photolysis of Ib and Ic afforded non-linear EDQ diagrams even in a neutral solution, the k_2/k_1 values for these derivatives are uncertain. We have estimated them to give a straight line with a gradient −1 against pH (Table 2).

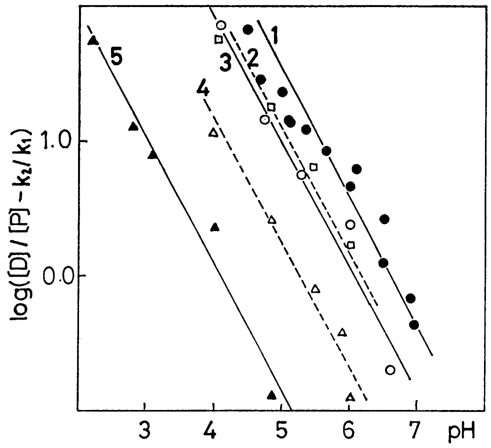


Fig. 4. pH-Dependency of photocyclization of diarylfumaronitriles; (1) diphenylfumaronitrile at 20 °C (—●—), (2) α-(*p*-anisyl)-α′-phenylfumaronitrile at 2 °C (--□--), (3) diphenylfumaronitrile at 2 °C (—○—), (4) α-(*p*-chlorophenyl)-α′-phenylfumaronitrile at 2 °C (--△--), (5) α-(*p*-cyanophenyl)-α′-phenylfumaronitrile at 2 °C (—▲—).

The spontaneous isomerization of VII to IV (path *b*) may involve an intramolecular process at least partially since the incorporation of solvent deuterium into the 9,10-dihydro compound occurs only partially.7) From the solid state photocyclization we have concluded that VII is a *trans* isomer.13) It is very likely that the intramolecular process occurs *via* the 1,3- or 1,7-sigmatropic shift of hydrogens of VII to afford the 9,10-dihydro derivative, which is a *trans* isomer.1)

Experimental

All the melting points are not corrected. Ultraviolet spectra were recorded on a Hitachi EPS-3T spectrometer, and monochromatic light was obtained on a JASCO CRM-FA Spectro Irradiator consisting of a 2 kW xenon lamp.

TABLE 3. α,β-DIARYLACRYLONITRILE $(p\text{-X-C}_6\text{H}_4\text{CH=C(CN)C}_6\text{H}_4\text{-Y-}p)$

	X	Y	Mp (°C)	Analysis (%)					
				Calcd			Found		
				C	H	N	C	H	N
a)	H	H	88a)	—	—	—	—	—	—
b)	Cl	H	102b)	—	—	—	—	—	—
c)	CN	H	170	83.45	4.38	12.17	83.49	4.20	12.32
d)	OMe	H	94—95c)	—	—	—	—	—	—
e)	CN	CN	260	79.98	3.55	16.16	79.91	3.48	16.63
f)	OMe	CN	161	78.44	4.65	10.76	78.12	4.46	10.71
g)	Me$_3$d)	H	102—105	87.41	6.93	5.66	87.54	7.17	5.58

a) 88 °C.14) b) 108 °C.15) c) 95 °C.16) d) 2,4,6-Trimethyl.

TABLE 4. α,α′-DIARYLSUCCINONITRILE $(\text{C}_6\text{H}_5\text{(CN)CH(CN)CHC}_6\text{H}_4\text{-X-}p)$a)

	X	Mp (°C)	Yield (%)	Analysis (%)					
				Calcd			Found		
				C	H	N	C	H	N
a)	H	236b)	97	—	—	—	—	—	—
b)	Cl	207—210	93	70.02	4.16	10.50	70.23	3.86	10.40
c)	CN	192	92	79.35	4.31	16.34	79.93	4.15	15.89
d)	OMe	200—202c)	94	—	—	—	—	—	—

a) Recrystallized from acetonitrile. b) 238—239 °C.17) c) 193 °C.16)

TABLE 5. DIARYLFUMARONITRILE $(\text{C}_6\text{H}_5\text{C(CN)=(CN)C}_6\text{H}_4\text{-X-}p)$ (I)

	X	Mp (°C)	Analysis (%)					
			Calcd			Found		
			C	H	N	C	H	N
a)	H	161a)	—	—	—	—	—	—
b)	Cl	141—142	72.60	3.43	10.59	72.58	3.60	10.52
c)	CN	161—164	79.98	3.55	16.46	80.38	3.09	16.66
d)	OMe	142—143	78.44	4.65	10.76	78.46	4.23	10.74

a) 161 °C.18)

TABLE 6. PHENANTHRENES (III)

	Substituents at			Mp (°C)	Analysis (%)					
					Calcd			Found		
	3	9	10		C	H	N	C	H	N
a)	H	CN	CN	290a)	—	—	—	—	—	—
b)	Cl	CN	CN	240	73.15	2.69	10.69	73.57	2.29	10.55
c)	CN	CN	CN	306—307	80.60	2.79	16.60	81.10	2.68	15.97
d)	OMe	CN	CN	240—241	79.05	3.90	10.85	78.68	3.98	10.73
e)	CN	CN	H	281—282	84.21	3.51	12.28	84.77	3.52	12.25

a) 295 °C.1)

Table 7. 9,10-Dihydrophenanthrenes (IV)

	Substituent at			Mp (°C)	Analysis (%)					
					Calcd			Found		
	3	9	10		C	H	N	C	H	N
a)	H	CN	CN	199—204[a]	—	—	—	—	—	—
b)	Cl	CN	CN	182—185	72.60	3.43	10.59	72.10	4.02	10.28
c)	CN	CN	CN	203—207	79.98	3.55	16.46	80.29	3.59	16.47
d)	OMe	CN	CN	154—155	78.44	4.65	10.76	77.93	3.88	10.50
e)	CN	H	CN	164—165	83.54	4.38	12.18	83.16	3.95	11.70

a) 199—204 °C.[1]

Table 8. Ultraviolet spectra of α-phenyl-α′-(*p*-substituted phenyl)fumaronitriles (I) in 50% aqueous ethanol

	X	λ_{max} ($\varepsilon \times 10^{-4}$) nm
a)	H	215 s (1.06), 238 (0.73), 331 (1.46)
b)	Cl	222 (1.37), 237 s (0.92), 337 (1.66)
c)	CN	330 (1.72)
d)	OMe	228 (1.31), 243 s (0.92), 290 (0.34), 365 (1.65)

Solvents were distilled before use.

α,β-Diarylacrylonitriles. The preparative method for α,β-diphenylacrylonitrile was employed.[14] The results are given in Table 3.

α,α′-Diarylsuccinonitrils. *(α,α′-Diphenylsuccinonitrile as a Typical Procedure)*: 90 g of potassium cyanide and 65 g of ammonium chloride were dissolved in 350 ml of water. The solution was added in one portion to a warm solution of 230 g of α,β-diphenylacrylonitrile in 750 ml DMF with shaking, and the mixture was allowed to stand for 1 h. Sufficient water was added to the mixture, the precipitate was filtered, washed with water and then with alcohol and dried. The crude product 268 g, mp 230—235 °C (lit,[17] mp 238—239 °C as *meso*-isomer), was satisfactory for further use. Results for diarylsuccinonitriles synthesized by this method are given in Table 4. The hydrocyanation of α-phenyl-β-(2,4,6-trimethylphenyl)acrylonitrile by this procedure was unsuccessful.

Diphenylfumaro- and Maleonitrile. A sodium methoxide solution prepared by dissolving 37.5 g sodium in 300 ml methanol was added dropwise under vigorous stirring to 197 g iodine and 180 g crude α,α′-diphenylsuccinonitrile in 500 ml THF. At the end of the addition the color of iodine faded with a rise of temperature of the mixture. After stirring for 1 h the solvent was evaporated, and the reaction mixture was treated with a large amount of water. The precipitated crystals were filtered, washed with water, twice with cold methanol and dried. The crude product weighed 132 g and were recrystallized from ethanol to yield 84 g crude diphenylfumaronitrile which was recrystallized once more from ethanol. Mp 159—160 °C (lit,[18] mp 161 °C). The combined ethanol filtrates were condensed to give 25 g crude diphenylmaleonitrile of mp 112—130 °C which was repeatedly recrystallized from ethanol until the mp became constant. The maleonitrile of mp 133—134 °C (lit,[19] mp 135 °C) weighed 16 g. α-Phenyl-α′-(*p*-substituted phenyl)-succinonitriles were oxidized in a similar manner to the procedure mentioned above. The crude products showed a wide range of mp, but the isolation of diarylmaleonitriles was not attempted. The results are summarized in Table 5. The UV spectra of diarylfumaronitriles obtained are given in Table 8.

p,p′-Dicyanostilbene. The compound was synthesized according to the method of Fu and Sah.[20] Mp 277—279 °C.

9,10-Dicyanophenanthrenes. A solution of 250 mg of diarylfumaronitrile in 100 ml of dichloromethane in a Pyrex flask was irradiated in the presence of 10 mg of iodine with a 450 W high pressure mercury lamp for 8 h. After the solvent had been evaporated, the crude product was chromatographed on alumina by means of dichloromethane as an eluent. The phenanthrenes were then recrystallized from methyl ethyl ketone. The results are given in Tables 6 and 9.

9,10-Dihydro-9,10-dicyanophenanthrenes. An ethanol (100 ml) solution of 250 mg diarylfumaronitrile was irradiated in a Pyrex flask with a 450 W high pressure mercury lamp under argon stream for 14 h. After the solvent had been evaporated, the residual crystalline product was recrystallized several times from ethanol. The dihydro compounds obtained are given in Table 7. The UV data are given in Table 10.

Isolation of Diphenylmaleonitrile in Photoisomerization. Two

Table 9. Ultraviolet spectra of the phenanthrenes (III) in 50 (%) aqueous ethanol

	Substituents at			λ_{max} ($\varepsilon \times 10^{-4}$) nm
	3	9	10	
a)	H	CN	CN	238 (3.47), 252 (3.45), 261.5 (3.80), 269 s (2.75), 325 (1.26), 339 (1.59)
b)	Cl	CN	CN	219 (2.26), 243 (4.62), 253.5 (3.80), 262.5 (4.05), 274 (2.50), 332 (1.50), 343 (1.72), 383 (0.20)
c)	CN	CN	CN	215 (2.12), 248 (4.65), 260 (3.70), 333 (1.18), 344 (1.38), 370 (0.24), 390 (0.27)
d)	OMe	CN	CN	219 (2.35), 253.5 (4.58), 263 s (3.36), 284 (1.94), 352 (1.43), 362 (1.49), 380 (1.18)
e)	CN	H	CN	232 (4.42), 250 (4.64), 281 (1.01), 313 (1.50), 324 (1.48), 347 (0.19), 368 (0.17).

TABLE 10. ULTRAVIOLET SPECTRA OF THE 9,10-DIHYDROPHENANTHRENES (IV) IN 50% AQUEOUS ETHANOL

	Substituents at			$\lambda_{\max}$ ($\varepsilon\times10^{-4}$) nm
	3	9	10	
a)	H	CN	CN	270(1.68)
b)	Cl	CN	CN	272(1.65)
c)	CN	CN	CN	233(3.36), 239(2.48), 271(1.58)
d)	OMe	CN	CN	234(3.02), 241(3.26), 272(1.63)

grams of diphenylfumaronitrile was dissolved in 150 ml 1,2-dichloroethane in a Pyrex flask and irradiated for 3 h with a mercury lamp. The solvent was evaporated to dryness, and the residue was recrystallized from ethanol to give crude starting material of mp 140—158 °C as needles. The filtrate was evaporated, the crystalline residue of mp 114—132 °C was recrystallized repeatedly from benzene-hexane to yield needle-like crystals of mp 132—134 °C. Identification was performed by mixture mp and UV absorption spectra.

Solvent Effect on the Yield of 9,10-Dicyanophenanthrene. Solutions of diphenylfumaronitrile in various solvents (5×10^{-5} M) were irradiated with 330 nm light until no more spectral change took place. The yield of 9,10-dicyanophenanthrene was calculated from the absorbance at 325 nm. The spectrum of the photoproduct in acidic solution was practically identical with that of 9,10-dihydro-9,10-dicyanophenanthrene.

Irradiation of 9,10-Dihydro-9,10-dicyanophenanthrene with Light of 270 nm. When an aerated solution of 9,10-dihydro compound in ethanol (5×10^{-5} M) was excited with 270 nm light, the absorbance at 269 nm decreased slowly with increase in the absorbance at 321 and 334 nm. The latter peaks are due to 9,10-dicyanophenanthrene.

Examination of EDQ diagrams[9] *of the Photolysis of Diarylfumaronitrile at Various pH.* The buffered solutions employed consist of citrate-phosphate-borate system. To a 25 ml buffer solution (0.01 M) was added *ca.* 10 ml ethanol with shaking, and then 5 ml 8×10^{-4} M ethanol solution of diarylfumaronitrile and finally ethanol in order to adjust the volume of the solution to 50 ml. A solution (4 ml) placed in a quartz cell (10×10 mm) was irradiated with 330 nm light at room temperature, and the UV spectrum was measured at intervals. The remaining sample solutions were subjected to pH measurement. Examination of EDQ diagram was carried out at pH 4.0, 5.0, 7.0, and 9.0.

Measurement of pH-Dependency of the Photoproduct Distribution. A cylindrical Pyrex cell containing 10 ml of the buffered solution was immersed in a thermostatted bath and irradiated through a quartz widnow with a 450 W mercury lamp until no more spectral change was observed. The irradiation time was *ca.* 5 min. The absorption spectra of the products at various pH showed isosbestic points. Since the prolonged irradiation caused gradual disappearance of 3,9,10-tricyanophenanthrene in aqueous ethanol, its yield was estimated by extrapolation. When buffered solutions of α-phenyl-β-(*p*-cyanophenyl)acrylonitrile (4.3×10^{-5} M) in aqueous ethanol were irradiated in a similar manner the absorption maxima at 313 and 324 nm due to 3,9-dicyanophenanthrene decreased and those at 272 and 241 nm due to 9,10-dihydro-3,9-dicyanophenanthrene increased with decrease in the pH of solutions. No isosbestic point appeared in the spectra of the irradiated solutions at various pH, the composition of the products being more complicated. No maxima due to the phenanthrene was observed at pH less than 4.

Observation of Colored Intermediate. A solution of diphenylfumaro- or maleonitrile (*ca.* 10^{-3} M) was irradiated with 320 nm light. Coloration was observed in chloroform, carbon tetrachloride, ethyl acetate, benzene, and toluene. The absorbance of the intermediate at 480 nm in toluene was recorded at intervals and found to decay following first order kinetics. The half lifetime was 100 s at room temperature.

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References

1) M. V. Sargent and C. J. Timmons, *J. Chem. Soc.*, **1964**, 5544.

2) F. B. Mallory, C. S. Wood, J. J. Gordon, L. C. Linquist, and M. L. Savitz, *J. Am. Chem. Soc.*, **84**, 4362 (1962).

3) W. H. Moore, D. D. Morgan, and F. R. Stermitz, *J. Am. Chem. Soc.*, **85**, 829 (1963).

4) F. B. Mallory, C. S. Wood, and J. T. Gordon, *J. Am. Chem. Soc.*, **86**, 3094 (1964).

5) K. A. Muszkat and E. Fischer, *J. Chem. Soc., B*, **1967**, 662.

6) As a preliminary report; S. Watanabe and K. Ichimura, *Chem. Lett.*, **1972**, 35.

7) R. Srinivasan and J. N. C. Hsu, *J. Am. Chem. Soc.*, **93**, 2816 (1971).

8) R. Stewart and D. J. Kroeger, *Can, J. Chem.* ,**45**, 2173 (1967).

9) G. Quinkert, *Angew. Chem.*, **84**, 1157 (1972).

10) The process of both appearance and disappearance of the intermediate (VII) in Eq. 1 can not be taken into consideration in the EDQ diagram examination, since VII was not observed UV-spectroscopically under the experimental conditions used.

11) G. S. Hammond, J. Saltiel, A. A. Lamola, N. J, Turro, J. S. Bradshaw, D. O. Cowan, R. C. Counsell, V. Vogt, and C. Dalton, *J. Am. Chem. Soc.*, **86**, 3197 (1964).

12) T. D. Doyl, N. Filipescu, W. R. Benson, and D. Banes, *J. Am. Chem. Soc.*, **92**, 6371 (1970).

13) K. Ichimura and S. Watanabe, *Tatrahedron Lett.*, **1972**, 821.

14) S. Wawzonek and E. M. Smolin, *Org. Synth.*, Coll. Vol. III, 715 (1955).

15) Beilsteins Handbuch der Organischen Chemie, Vol. 9, 693 (1926).

16) K. Brand and L. Loehr, *J. Prakt. Chem.*, **109**, 359 (1925).

17) R. B. Davis and J. A. Ward, *Org. Synth.*, Coll. Vol. IV, 392 (1963).

18) J. T. Thurston and R. L. Shriner, *J. Org. Chem.*, **2**, 183 (1937).

19) M. V. Sargent and C. J. Timmons, *J. Chem. Soc.*, **1964**, 2222.

20) S. -C. Fu and P. P. P. T. Sah, *J. Am. Chem. Soc.*, **64**, 1482 (1942).