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THE EFFECT OF pH ON THE PHOTOCYCLIZATION OF DIPHENYLFUMARODINITRILE

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The photocyclization of diphenylfumarodinitrile was found to suffer the pH effect. The yield of 9,10-dicyanophenanthrene decreases with decrease in pH of the solution.

The oxidative photocyclization of stilbenes to the phenanthrenes has been investigated extensively.1) Sargent and Timmons have reported the formation of 9,10-dihydrophenanthrenes along with the oxidized phenanthrenes through photocyclization of some stilbene derivatives substituted by the electron-withdrawing groups on the central double bond.2)

Recently, Srinivasan and Hsu have proposed the radical mechanism for this type of photocyclization.3) We now wish to report the ionic behavior of the photocyclization of diphenylfumarodinitrile (1).

The photoreaction was carried out in 1 : 1 v/v aqueous ethanol solution of 1 (8.0×10^{-5} M) which is exposed to the air. The concentration of hydrogen ion in the solutions was adjusted by the suitable buffers (0.005 M). The absorption spectra of 1 at various pH less than 10 were unchanged. Since the product distribution was found to be also dependent on temperature and 9,10-dihydro-9,10-dicyanophenanthrene (5) is transformed to 9,10-dicyanophenanthrene (4) by 270 nm excitation, the solutions of 1 were then irradiated by 450 W high pressure mercury lamp in a cylindrical reaction cell immersed in a temperature controlled bath with a quartz window. The irradiation time was about 5 min where no more spectral change occurs. The absorption spectra of the products at various pH at 20°C show that only 5 is formed below pH ca. 4, and the isosbestic points appear at 265 nm and 290 nm. The peaks at 326 nm and 339 nm due to the phenanthrene (4) increase with increase in pH of the solutions, and the ratio of absorbance at these two wave lengths is constant in every absorption spectrum. These facts indicate that only 4 and 5 are concerned in the product distribution. The yield of 4 is estimated by the absorbance at 329 nm and plotted against pH, as shown in Fig. 1.

During the irradiation of diphenylfumaro (1)- or maleodinitrile* (2) in such solvents as aromatic hydrocarbons and chloroalkanes, we observed the red coloration of λ_{max}= 480 nm (in toluene). Although there was no observation of such coloration in ethanol at room temperature, the solution of diphenylmaleodinitrile was found to be faintly colored at dry ice-alcohol temperature. We ascribe this transient absorption to the intermediary unstable dihydrophenanthrene (3), just as in the case of stilbene, where yellow coloration (λ_{max}=447 nm) has been reported.1c)

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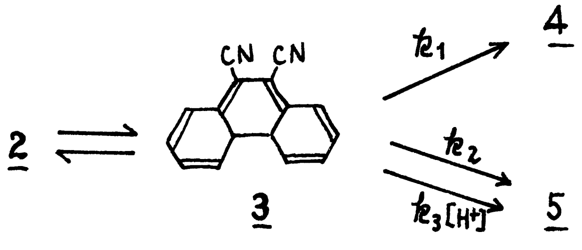
* This was isolated by the photoisomerization of 1 as crystals of mp 134-135°C (reported mp 134°C).4)

The intermediate (probably 3) could be isomerized to 5 by proton along with the spontaneous isomerization to 5 and the formation of 4, as shown in the following scheme.



We obtain then in the region pH < 7

$$\log ([D]/[P]-k_2/k_1) = \log (k_3/k_1)-pH$$

where [D] and [P] are the yields of 5 and 4, respectively. k_2/k_1 is assumed to be [D]/[P] at pH≒7 and 2.77 in our experiment. As shown in Fig. 2, log ([D]/[P]-2.77) was found to be nicely correlated to pH with a gradient -1.

The effect of pH on the photocyclization shown in Fig. 1 may be thus caused by the acid catalysed isomerization of 3 to 5. The unstable intermediate (3) in the ground state could be protonated at the nitrile group, the tertiary allylic hydrogen could then be eliminated to aromatize one of the rings, and proton at nitrile group rearranges to benzylic position. This process is repeated readily once more to complete the isomerization.

The possibility that proton interacts with certain molecule(s) in the excited state, however, could not be excluded. The studies on the extension of the pH effect on other systems are now in progress. We will describe the photochemistry of this type of cyclization in more detail in near future.

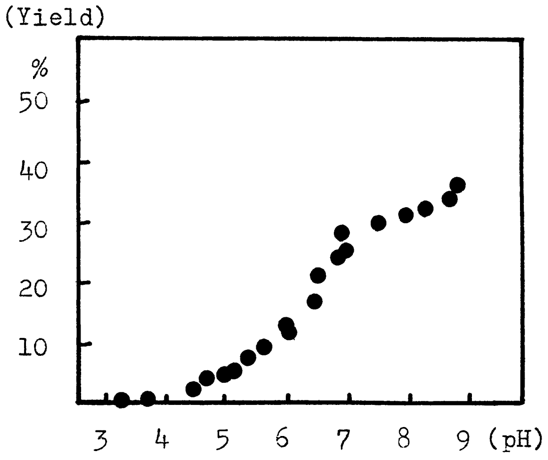


Fig. 1. Dependence of the yield of 9,10-dicyanophenanthrene (4) upon pH.

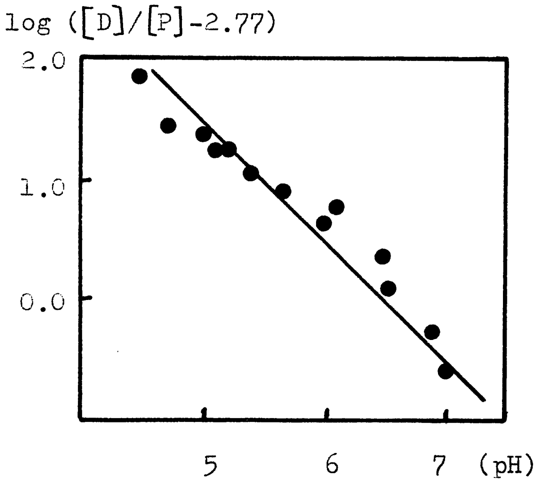


Fig. 2. Correlation of product ratio to pH.

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