Short Communication

Evidence for the dihydrophenanthroimidazole intermediate in the photocyclization of 4,5-diphenylimidazole

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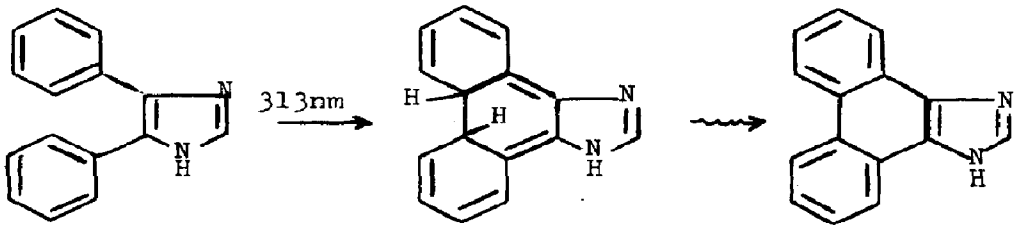
In a previous study from this laboratory we demonstrated the photocyclization of 4,5-diphenylimidazole (DPI) to 9,10-phenanthroimidazole (PI) [1]. The process was shown to be a singlet reaction; however, we were unable to observe the dihydrophenanthroimidazole (DHPI) as the intermediate species, which is usually observed in the photocyclization of *cis*-stilbenes and related molecules [2 - 4].



DPI DHPI PI

It had been suggested that the process may involve free radicals since the photocyclization to DHPI was observed in degassed as well as in air-saturated solutions. That oxygen may assist the conversion to the totally aromatic photoproduct was evident in the larger quantum yield measured for air-saturated relative to degassed solutions [1]. With the intent to pursue this mechanism further we have undertaken a flash photolysis study of DPI in isopropyl alcohol and acetonitrile.

The flash photolysis of an air-saturated solution of DPI in isopropyl alcohol results in a transient absorption in the wavelength region 380 - 530 nm, which is shown in Fig. 1. The transient has a lifetime of 1.2 ms and exhibits peaks at 400 and 475 nm. We assign this transient as the DHPI intermediate, since (1) it appears in the same wavelength region as that of 4*a*,4*b*-dihydrophenanthrenes [2], (2) its lifetime is too long for it to be due to triplet–triplet absorption and (3) it is absent when all the DPI has been converted to PI. It was determined that approximately 0.7% decomposition

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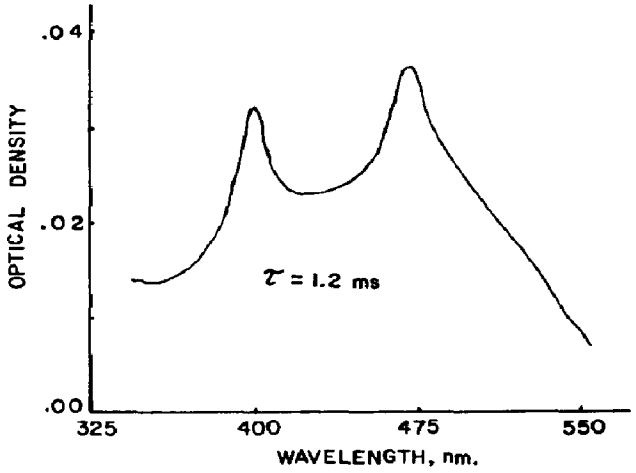

Fig. 1. Flash photolysis transient observed for an air-saturated solution of 1.4×10^{-4} M DPI in isopropyl alcohol.

occurred per flash (180 J). The same transient is observed when DPI is flashed in air-saturated acetonitrile as the solvent, where the disappearance of DPI was 2.5% per flash. In both solvents the kinetic decay of the transient was first order. Flashing vacuum-degassed solutions of DPI in these two solvents resulted in a small increase in transient absorption, but with no significant change in its lifetime.

The UV absorption changes resulting from the flash photolysis of an air-saturated solution of 1.4×10^{-4} M DPI in isopropyl alcohol are summarized in Fig. 2, where it is seen that the disappearance of DPI is accompanied by the growth of PI as the photoproduct.

The present study illustrates that photocyclization intermediates can often be missed in steady state photolysis. It is fortuitous that in the de-

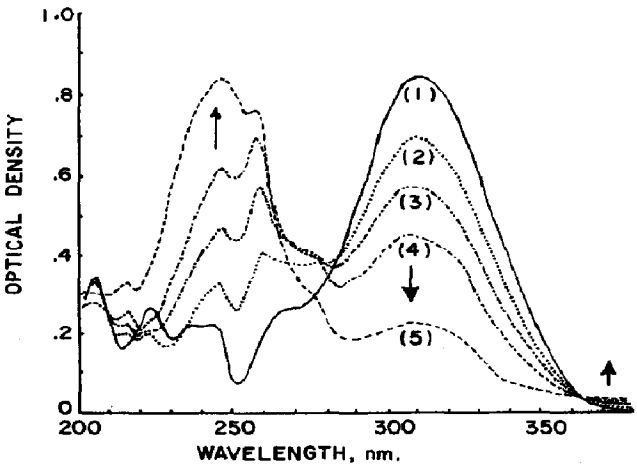

Fig. 2. UV spectral changes resulting from the flash photolysis of 1.4×10^{-4} M DPI in isopropyl alcohol (air saturated): curve 1, initial spectrum; curve 2, after 15 flashes; curve 3, after 30 flashes; curve 4, after 45 flashes; curve 5, after 100 flashes.

gassed photocyclization of *cis*-stilbene to phenanthrene the 4*a*,4*b*-dihydrophenanthrene intermediate (absorbing at about 450 nm) lives long enough to be seen in conventional photolysis experiments. In the case of DPI, however, the intermediate has a lifetime of 1.2 ms and necessitates a flash photolysis experiment.

DPI was purified by recrystallizing from benzene and then ethanol to yield white needles. Spectrograde isopropyl alcohol and acetonitrile, obtained from Burdick & Jacksons Labs., were used as received. A 20 μs flash apparatus was used with an energy input of about 180 J per flash. UV absorption spectra were measured using a Cary model 14 spectrophotometer.

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