

THE PHOTOCHEMICAL REACTION OF 9,10-DIAZAPHENANTHRENE IN ACIDIC SOLUTION

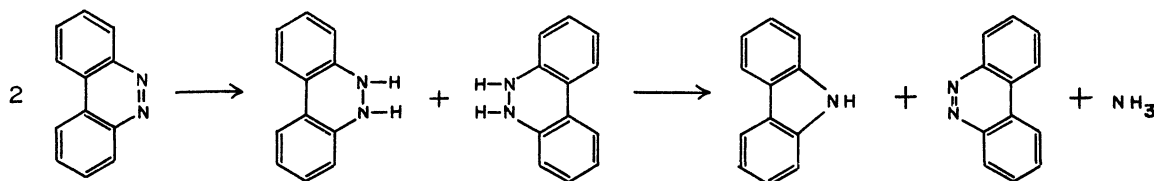
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The photochemical reaction of 9,10-diazaphenanthrene (DAP) was investigated in the acidic aqueous 2-propanol under nitrogen. It has been found that with ultraviolet irradiation (366 nm) DAP changes into carbazole. On the other hand, it was deduced that 2,2'-diamino-biphenyl was produced with visible light irradiation.

Hitherto, few reports are available concerning the photochemical reaction of 9,10-diazaphenanthrene (DAP). In this report, we deal with the photochemical reaction of DAP in a mixed solvent of 2-propanol-water (11:2) containing HCl (3.75 N) under nitrogen.

Figure 1 shows the spectral change of the solution with ultraviolet irradiation (366 nm). Curve III in Fig. 1 seems to be the absorption spectrum of a product. The product was isolated by evaporating the solvent from the neutralized solution under reduced pressure, and the white crystalline substance was obtained by recrystallization from ethanol, mp 245-246°C. From UV, IR, melting point, and elementary analysis (Found: C, 87.0; H, 5.2 %) of the isolated compound, the product is identified as carbazole.<sup>1,2)</sup> Irradiation for 120 min led to the production of carbazole in about 80 % yield. Since the liberation of ammonia gas takes place on heating the irradiated solution, the following reaction scheme may be reasonable for the carbazole formation.



On the other hand, visible light irradiation on the solution of DAP causes the spectral change which is different from that shown in Fig. 1. Apparently, in this case, carbazole is not formed. The short period irradiation within 30 min leads the production of an unstable compound which easily reverts to DAP by blowing oxygen into the solution or by neutralization of the solution. On the other hand, the long period irradiation results in the production of a compound which has very weak absorption band in the acidic solution. The neutralized solution shows the absorption bands at 246 nm (shoulder) and 298 nm as shown in Fig. 2. From the spectral resemblance<sup>3)</sup>, the product with visible light irradiation can be tentatively considered to be 2,2'-diaminobiphenyl. A detailed study is in progress.

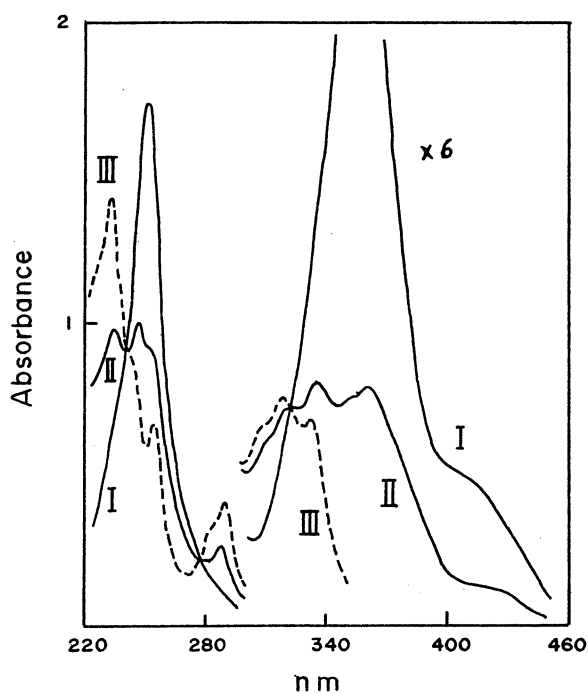


Fig. 1. Spectral change of the acidic solution with ultraviolet irradiation. I=0 min, II=60, III=120

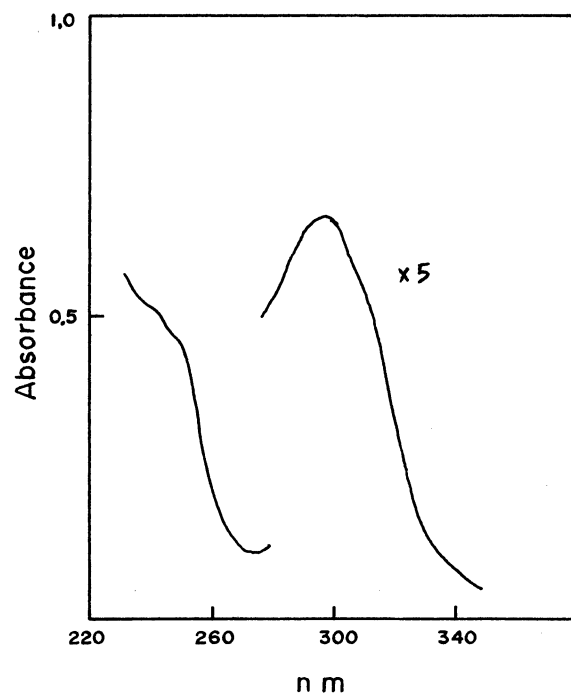


Fig. 2. The absorption spectrum of the neutralized solution after visible light irradiation (420 min).

#### References

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