

THE SYNTHESIS OF A PHENANTHRIDENE FROM AN AROMATIC
SCHIFF BASE BY A PHOTOOXIDATIVE RING CLOSURE

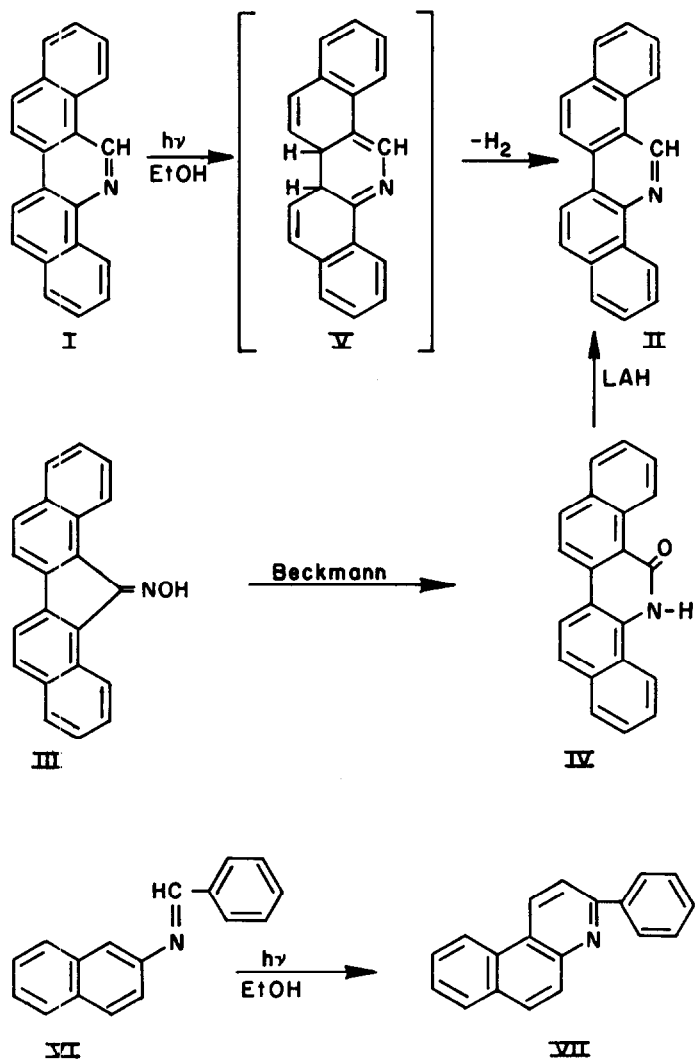
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The conversion of stilbenes into phenanthrenes by an oxidative photochemical process has been the object of considerable study;¹ the related photochemical conversion of azobenzene to phenazone has also been described.² We wish now to report the first example of an analogous synthesis of a phenanthridene from an aromatic Schiff base.

Ultraviolet irradiation of Schiff base I (formed from α -naphthylamine and α -naphthaldehyde)³ in ethanol in the presence of air afforded, in 40% yield, the previously unreported dibenzo[c,i]phenanthridene (II), m.p. 270°. (Found: C, 90.26; H, 4.75; N, 5.21. Calcd. for C₂₁H₁₃N: C, 90.29; H, 4.69; N, 5.02.) The ultraviolet spectrum (in dioxane) showed λ_{max} 230 m μ ($\epsilon = 55,000$), 252 (84,000), 273 (86,000), 282 (92,000), 315 (14,000), 330 (13,000), 355 (6,000), and 374 (8,200).

The structure of dibenzo[c,i]phenanthridene (II) was confirmed by an independent synthesis. Thus, the reaction of dibenzo[a,i]fluorenone⁴ with hydroxylamine hydrochloride in refluxing pyridine gave, in 83% yield, dibenzo[a,i]fluorenone oxime (III), m.p. 210-215° (decomp.). (Found: C, 85.59; H, 4.49; N, 4.85. Calcd. for C₂₁H₁₃NO: C, 85.40; H, 4.44; N, 4.74.) Beckmann rearrangement of oxime III in polyphosphoric acid at 130° afforded, in 65% yield, crude dibenzo[c,i]phenanthridone (IV) as a sparingly soluble, light brown powder, m.p. 300°. Compound IV, without further purification, was reduced with lithium aluminum hydride in refluxing dioxane to give, after careful chromatography on alumina, dibenzo[c,i]phenanthridene (II) in 36% yield; samples of compound II prepared in this manner were identical by mixed melting point determination and by infrared and ultraviolet comparison with those prepared by the photolysis reaction.



The photochemical conversion of Schiff base I into phenanthridene II could be effected by light in the energy range 2800-3200 Å (compound I exhibits strong absorption in this region).⁵ Mechanistic evidence concerning the detailed course of this reaction is not yet available, but it seems likely that, in analogy to the stilbene-phenanthrene transformation, an unstable dihydrophenanthridene (V) may be an intermediate.⁶ Further work on the nature and the scope of photooxidative reactions of Schiff bases is in progress.

The ultraviolet irradiation of Schiff base VI (formed from benzaldehyde and β-naphthylamine) in ethanol solution and in the presence of air has been reported recently.⁷ The reaction product, 2-phenyl-5,6-benzoquinoline (VII) is formed by a novel process involving the incorporation of a C₂ fragment derived from the solvent into the skeletal system of the Schiff base, but this transformation would appear to be quite unrelated to that reported by us here.

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REFERENCES

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5. For an interpretation of the ultraviolet spectrum of benzaniline and related compounds see: P. Brocklehurst, *Tetrahedron*, 18, 229 (1962).
6. The conversion of I into II has been effected in hydrocarbon solvents as well as in ethanol. In benzene solution in the presence of dissolved oxygen II was obtained in 15% yield, whereas in a degassed benzene solution, the formation of II from I was totally suppressed. This result is consistent with the intermediacy of the dihydrophenanthridene V in the reaction.
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