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THE PHOTOCYCLIZATION OF ANILS TO PHENANTHRIDINES*

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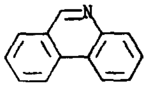
We recently reported that N-benzylideneaniline (I) failed to undergo oxidative photocyclization to phenanthridine (II) under the conditions that stilbene is readily converted photochemically to phenanthrene.[1] Similar observations have been reported by others.[2,3,4]

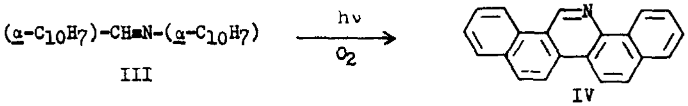
$C_6H_5\text{-}CH{=}N\text{-}C_6H_5$

I



II

Subsequently, the successful photoconversion of the anil III to the corresponding phenanthridine derivative IV was described.[5]



$(\underline{\alpha}\text{-}C_{10}H_7)\text{-}CH{=}N\text{-}(\underline{\alpha}\text{-}C_{10}H_7) \xrightarrow[O_2]{h\nu}$

III

IV

This unexpected discrepancy has led us to re-examine our earlier work, and in so doing to confirm that ultraviolet irradiation of 4×10^{-3} M solutions of I in cyclohexane, benzene, or ethanol in quartz or Pyrex tubes at 30-40° in the presence of dissolved oxygen or iodine leads to the destruction of I

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* Photochemistry of Stilbenes. V. For part IV see C. S. Wood and F. B. Mallory, J. Org. Chem. 29, 3373 (1964).

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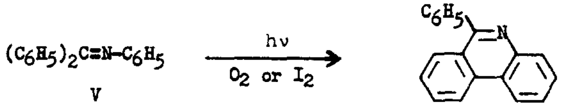
without producing detectable[*] amounts of II at any stage.

We believe that this observed failure of I to undergo photoconversion to II is satisfactorily accounted for stereochemically. By analogy with the photocyclization of stilbene, which has been demonstrated[**] to occur only following photoexcitation of the *cis* isomer and not the *trans* isomer, we suggest that the photocyclization of I might also be expected to occur only by photoexcitation of the *cis* isomer. It has been shown recently[3,6] that the thermal *cis*→*trans* isomerization of I is extraordinarily fast, the half life of the *cis* isomer being about 1 sec. at room temperature; thus, although *trans*-I is known to undergo photoisomerization to *cis*-I, the photostationary *cis*/*trans* concentration ratio has been found to be extremely small except at low temperatures.[3,6]

This stereochemical interpretation for the lack of photocyclization of I has been supported by two types of experiment. First, by irradiating solutions of I that were maintained at 10° in order to decrease the thermal *cis*→*trans* rate and hence increase the photostationary concentration of the *cis* isomer, it was possible to detect[*] up to 2% conversion to II during the early stages of irradiation.[***] Second, *N*-diphenylmethyleneaniline (V), a compound whose photocyclization is not subject to the type of stereochemical prohibition suggested above for the photocyclization of I, was found to be converted photochemically to 6-phenylphenanthridine (VI) under


$(C_6H_5)_2C{=}N{-}C_6H_5 \xrightarrow[O_2 \text{ or } I_2]{h\nu}$

V VI

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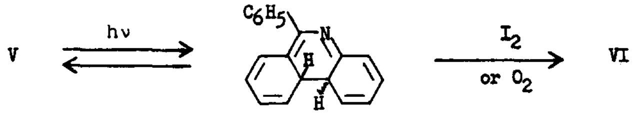
[*] Gas-liquid chromatography with flame ionization detection was used under conditions that 0.1% conversion of I to II would easily have been observed.

[**] For pertinent references, see Ref. 1.

[***] Continued irradiation resulted in the destruction of both I and II; no characterizable products were obtained.

the irradiation conditions normally employed for the conversion of triphenylethylene to 9-phenylphenanthrene[1] except that the required irradiation time was much greater. Thus, a solution of 322 mg. (1.25 mmole) of V and 16 mg. (5 mole-%) of iodine in 250 ml. of redistilled cyclohexane was stirred magnetically and irradiated internally for 67 hr. with a modified 400-watt G. E. mercury lamp[1] contained in a water-cooled quartz probe. The crude product was purified by chromatography on alumina using 60-70° ligroin as eluant, by recrystallization from 30-40° petroleum ether, and by vacuum sublimation to give 146 mg. (46%) of 6-phenylphenanthridine (VI), m.p. 105.0-106.0° (lit.[7] m.p. 106°); the picrate melted at 251.0-252.5°(dec.) (lit.[7] m.p. 251°(dec.)).

The photoconversion of V to VI does not occur in the absence of iodine and oxygen in thoroughly degassed cyclohexane solutions. This suggests that the photoreaction proceeds by way of an intermediate dihydrophenanthridine derivative (VII) analogous to the dihydrophenanthrenes that are considered to be intermediates in the photocyclizations of stilbenes.[1]



VII

The trans configuration is suggested for the two tertiary hydrogens in VII by analogy with the tentative assignment of trans stereochemistry made previously[1] for the related dihydrophenanthrenes; there is increasing theoretical support for this assignment.[8,9]

Quantum yields were measured in order to compare quantitatively the efficiency of photocyclization of V with that of triphenylethylene. Magnetically stirred, 3-ml., 5×10^{-3} M solutions of V and of triphenylethylene were irradiated in a 1-cm. quartz cell at 25° using 313 mμ light from a mercury arc and a grating monochromator. The extent of conversion to VI and 9-phenylphenanthrene, respectively, was in the range of 0.1-10% and was determined by gas-liquid chromatography with disc integration. The light intensity was measured by ferrioxalate actinometry.[10] The quantum yield for formation of 9-phenylphenanthrene was found[11] to be 5×10^{-2} and the quantum yield for formation of VI was found to be 3×10^{-5}; the latter value is known only approximately owing to the experimental difficulties in determining a quantum yield of such a small magnitude.

The fact that the quantum yield for photocyclization of V is more than three orders of magnitude smaller than that for triphenylethylene can be given various interpretations. For example, it might be that stilbenes of related molecules undergo this type of cyclization with reasonable efficiency (i.e., with quantum yields greater than 10^{-2}) only when they are in their lowest $\pi \rightarrow \pi^*$ excited singlet states ($^1\pi,\pi^*$) as has been argued previously,[1] and that in the case of the anil V the lowest excited singlet state is of the $n \rightarrow \pi^*$ type ($^1n,\pi^*$) such that the lifetime of the $^1\pi,\pi^*$ excited molecules would be almost prohibitively short as far as cyclization is concerned owing to a rapid internal conversion to give $^1n,\pi^*$ excited molecules. Unfortunately, we are unable to provide support for this interpretation by direct and definitive spectroscopic evidence that the lowest-energy excited singlet state of V is its $^1n,\pi^*$ state; thus, although the maximum of the long wave length band in the ultraviolet absorption spectrum of V does undergo a shift in 95% ethanol solution (333 mμ) relative to cyclohexane solution (342.5 mμ) that is in the direction characteristic for an $n \rightarrow \pi^*$ absorption band, the molar absorptivity at the maximum (2560 l. mole^{-1} cm.$^{-1}$ in 95% ethanol, 2420 l. mole^{-1} cm.$^{-1}$ in cyclohexane) seems too high for an $n \rightarrow \pi^*$ transition. However, the assignment[12] of the $^1n,\pi^*$ state as the lowest-energy excited singlet state of the related anil I gives indirect support for the interpretation given above for the low photoreactivity of V. This interpretation is also consistent with the report[13] that phenanthridine (II) is produced in substantial yield by carrying out the irradiation of I in 98% sulfuric acid as a solvent; the species undergoing cyclization under these conditions is probably the cation which is derived from I by protonation on nitrogen and which therefore would not have a $^1n,\pi^*$ state as its lowest excited singlet state.

In view of the extremely small quantum yield for the photoconversion of V to VI, it is not at all unreasonable that this photoreaction escaped discovery in previous investigations[3,6,14] in which solutions of V were irradiated.

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REFERENCES

(1) F. B. Mallory, C. S. Wood, and J. T. Gordon, J. Amer. Chem. Soc. 86, 3094 (1964).

(2) P. Hugelshofer, J. Kalvoda, and K. Schaffner, Helv. Chim. Acta 43, 1322 (1960).

(3) E. Fischer and Y. Frei, J. Chem. Phys. 27, 808 (1957).

(4) G. M. Wyman, Chem. Rev. 55, 625 (1955).

(5) M. P. Cava and R. H. Schlessinger, Tetrahedron Letters, 2109 (1964).

(6) D. G. Anderson and G. Wettermark, J. Amer. Chem. Soc. 87, 1433 (1965); G. Wettermark, J. Weinstein, J. Sousa, and L. Dogliotti, J. Phys. Chem. 69, 1584 (1965).

(7) C. L. Arcus and M. M. Coombs, J. Chem. Soc. 4319 (1954).

(8) R. B. Woodward and R. Hoffmann, J. Amer. Chem. Soc. 87, 395 (1965).

(9) H. C. Longuet-Higgins and E. W. Abrahamson, J. Amer. Chem. Soc. 87, 2045 (1965).

(10) C. G. Hatchard and C. A. Parker, Proc. Roy. Soc. A235, 518 (1956).

(11) F. B. Mallory, J. T. Gordon, and C. S. Wood, *J. Amer. Chem. Soc*. **85**, 828 (1963); F. B. Mallory and S. P. Varimbi, unpublished results.

(12) H. H. Jaffé, S.-J. Yeh, and R. W. Gardner, *J. Mol. Spectroscopy* **2**, 120 (1958).

(13) G. M. Badger, C. P. Joshua, and G. E. Lewis, *Tetrahedron Letters*, 3711 (1964).

(14) W. H. Saunders, Jr., and E. A. Caress, *J. Amer. Chem. Soc*. **86**, 861 (1964).