

to 4 provides support for the first step of the proposed pathway.¹³

(13) Possible mechanisms for the CF_3COOH transformations will be discussed in our full paper.

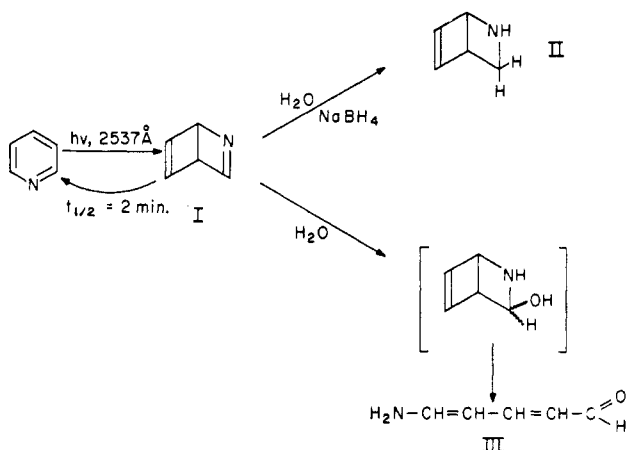
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Photochemistry of Nitrogen Heterocycles. Dewar Pyridine and Its Intermediacy in Photoreduction and Photohydration of Pyridine¹

Sir:

We wish to report (1) that photoisomerization of pyridine to a Dewar pyridine, 2-azabicyclo[2.2.0]hexa-2,5-diene (I), occurs in the liquid phase at 2537 Å; (2) that photoreduction of pyridine occurs in aqueous sodium borohydride, yielding 2-azabicyclo[2.2.0]hex-5-ene (II), and (3) that I is an intermediate in the formation of II, as well as in the photohydration² of pyridine to 5-amino-2,4-pentadienal (III). The Dewar pyridine, which is the first valence isomer of pyridine or its derivatives to be found,³ reverts completely to pyridine within 15 min at room temperature, but fortunately has a high activation energy, 16 kcal mol⁻¹, for rearomatization. The picolines and several lutidines also form thermally unstable photoisomers which are reduced by borohydride and hydrolyzed by water.



The formation and rearomatization of these photoisomers can be observed spectrophotometrically. The uv absorption of a $2.5 \times 10^{-4} M$ solution of pyridine in acetonitrile receiving $2.4 \times 10^{17} \text{ g cm}^{-2} \text{ min}^{-1}$ at 2537 Å decreases 7% in a 1-min irradiation and is restored quantitatively in the dark with a half-time of 2.5 min at 25°. (The rates of formation and decay of methylpyridine photoisomers are of the same magnitude.) The limiting concentration of I, 14%, reached upon further irradiation is lower than that expected in the absence of photochemical disappearance, suggesting

(1) Based on work performed under the auspices of the U. S. Atomic Energy Commission.

(2) (a) H. Freytag, *Chem. Ber.*, **69B**, 32 (1936), and references therein; (b) D. Abelson, E. Parthé, K. W. Lee, and A. Boyle, *Biochem. J.*, **96**, 840 (1965); (c) J. Joussot-Dubien and J. Houdard-Pereyre, *Bull. Soc. Chim. Fr.*, 2619 (1969).

(3) A photoproduct of 2-amino-5-chloropyridine was reported⁴ to be a Dewar isomer, but was subsequently shown⁵ to be a 1,4 dimer.

(4) E. C. Taylor, W. W. Paudler, and I. Kuntz, *J. Amer. Chem. Soc.*, **83**, 2967 (1961).

(5) E. C. Taylor and R. O. Kan, *ibid.*, **85**, 776 (1963).

that the calculated quantum yield of 0.05 may be lower than the true value (*vide infra*). At 0°, the Dewar pyridine is formed at a comparable rate but has a considerably longer half-life, 36 min. Its uv spectrum at this temperature, measured against a pyridine blank, shows only end absorption, $E_{2200} \approx 4000$.

The thermal and photochemical properties of I permit accumulation of moderate quantities in photolyses at low temperatures. An amount sufficient for nmr analysis was prepared by irradiating 50 mg of pyridine in 35 ml of *n*-butane for 45 min at -15° with a G8T5 germicidal lamp. The reaction mixture was processed by adding 300 mg of pyridine-*d*₅, removing solvent at -50°, and distilling the pyridine solution of I at -30°. In addition to the pyridine resonances, the nmr spectrum⁶ at -25° showed four multiplets of equal area at δ 4.03, 5.22, 6.51, and 6.54. These resonances were absent after the sample had been maintained at 25° for 15 min. On the basis of their chemical shifts and coupling constants⁷ they have been assigned to protons at positions 4, 1, 6, and 5, respectively. The resonance of the proton at position 3, indicated by the multiplicities of those at positions 1 and 4, would be expected to fall at lower field and be obscured by the large pyridine resonances.

When pyridine is irradiated at 2537 Å in aqueous NaBH_4 it disappears with a quantum yield of 0.07 and is not regenerated thermally. The initial product⁸ of such irradiations, extracted into ether, has an elution volume 0.7 that of pyridine on a Carbowax 20M (3%) polyethylenimine (1.7%) column⁹ at 70° and a parent mass of 81. It has been isolated by preparative glpc and identified as 2-azabicyclo[2.2.0]hex-5-ene (II) by its nmr spectrum and by its reduction with P-1 nickel boride catalyst¹⁰ to cyclobutanemethylamine¹¹ and piperidine. The nmr spectrum of II in CCl_4 shows a singlet (N-H) at δ 1.22 and multiplets at δ 2.93, 3.36, 3.51, 4.28, 6.32, and 6.51. These have been assigned¹² to protons at positions 3-*endo*, 4, 3-*exo*, 1, 5, and 6, respectively.

Photolysis of 3,5-lutidine in aqueous NaBH_4 yields a corresponding dihydro product, 4,6-dimethyl-2-azabicyclo[2.2.0]hex-5-ene. Its nmr spectrum shows singlets at δ 1.15 (N-H) and 1.20 (4- CH_3) and multiplets at δ 1.76 (6- CH_3), 3.02 (3_n), 3.21 (3_x), 3.76 (1), and 6.07 (5).

The intermediacy of I in the formation of II was shown by the fact that II was found when an aliquot of a briefly irradiated ether solution of pyridine was stirred with aqueous NaBH_4 immediately after irradiation, but was absent when another aliquot was similarly treated 10 min later.

Previous studies have shown that irradiation of aqueous pyridine at 2537 Å yields a product which

(6) Nmr spectra were taken at 100 Mc on a Varian HA-100 spectrometer. We are indebted to Mrs. Gail Ryan for these spectra.

(7) $J_{1,4} \approx J_{1,5} \approx J_{5,6} = 1.7 \text{ cps}$; $J_{1,3} \approx J_{1,5} \approx J_{3,4} = 0.7 \text{ cps}$.

(8) In irradiations continued to the virtual absence of pyridine an equal yield of 1,2,3,6-tetrahydropyridine and a small amount of piperidine are also found.

(9) J. R. L. Smith and D. J. Waddington, *J. Chromatog.*, **42**, 183 (1969).

(10) H. C. Brown and C. A. Brown, *J. Amer. Chem. Soc.*, **85**, 1005 (1963).

(11) Characterized by identity of glpc retentions and nmr spectrum with those of a sample prepared by reduction of cyclobutanecarboxamide with LiAlH_4 .

(12) Relevant coupling constants in cps are: $J_{1,4} = J_{5,6} = 2.6$; $J_{3n,4} = 2.2$; $J_{3x,4} = 7$; $J_{3n,3x} = 8$. The nmr spectrum of the dihydro product from pyridine-*d*₅ shows only three singlets in the ratio of 2:1:1 at δ 1.20, 2.89, and 3.52, respectively.