Tetrahedron Letters No.44, pp. 4389–4391, 1967. Pergamon Press Ltd. Printed in Great Britain.

REVERSIBLE PHOTOLYSIS OF PYRIDINE IN AQUEOUS SOLUTION

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(Received in UK 2 August 1967)

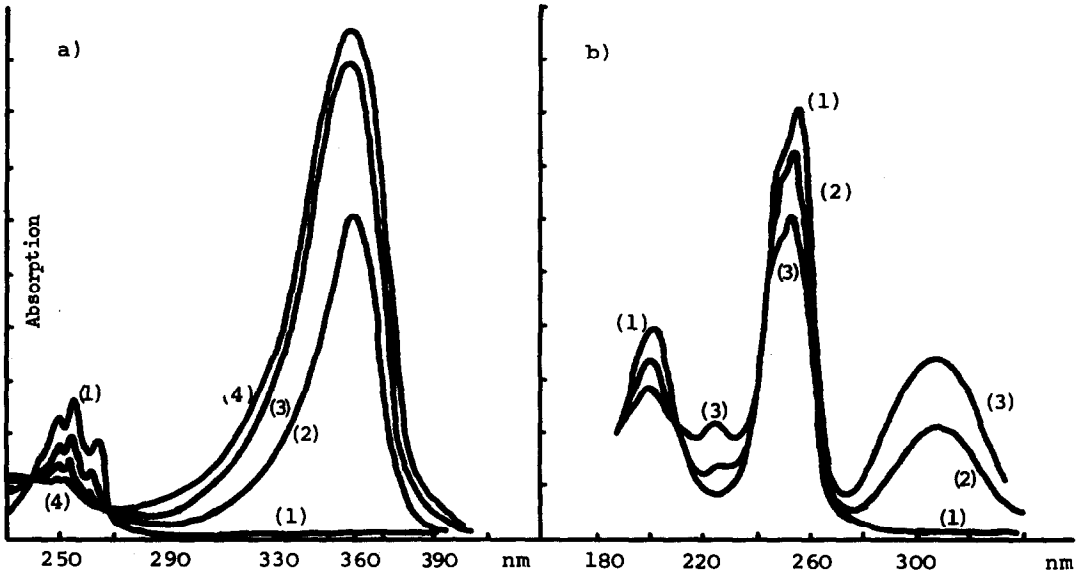
It is known since the work of FREYTAG (1) that under UV irradiation and in the presence of oxygen, pyridine in water or alcoholic solution is photolysed to a derivative of glutaconic aldehyde. In this reaction, the pyridine ring is opened between the nitrogen atom and the neighbour carbon atom. We have found that, under certain conditions, the first steps of the reaction are reversible in the dark.

When an aqueous solution of pyridine is irradiated with 256 nm light from a low pressure mercury arc one can easily follow spectroscopically the disappearance of the pyridine. At the same time appears a new structureless absorption band with a maximum at 360 nm if the solution is basic or at 306 nm if the solution is acid. This is illustrated on the figure, calling P 360 and P 306 the photoproducts giving the absorption maxima respectively at 360 and 306 nm.

The initial photoreaction occurs just as well in the presence or absence of dissolved oxygen, however oxygen gives rise to further reactions.

The quantum yield of formation for the photoproduct P 360 is .070 and is independent of light intensity or pyridine concentration in the range $1,2 \times 10^{-2}$ to 5×10^{-5} M l^{-1}.

The photoproducts P 360 and P 306 seem to be conjugate acid and base pair since it is possible to obtain either product from the other by simply



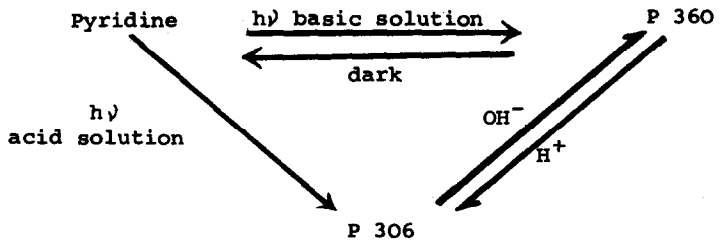
Photolysis of pyridine in aqueous solution by 256 nm light : a) in alkaline solution ; b) in acid solution - Spectra 1 are taken before irradiation, spectra 2, 3 and 4 after increasing time of irradiation.

changing the pH of the solution, however the reaction is slow.

Photoproduct P 306 is stable in the dark at room temperature whereas photoproduct P 360 regenerates pyridine in the dark and the photoreaction can be carried over again. The reverse reaction is temperature dependent, very slow but giving good yield of pyridine at low temperature, very inefficient at higher temperature.

In the presence of a large excess of acid another photoproduct appears, absorbing at 345 nm, but it is quickly transformed to product P 306.

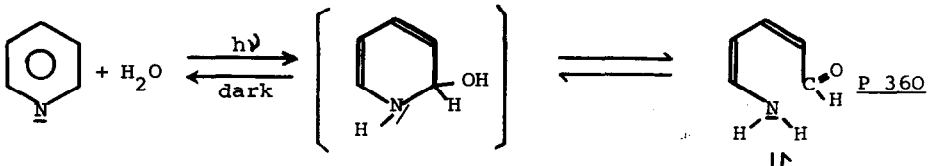
The different products obtained are schematically given below :



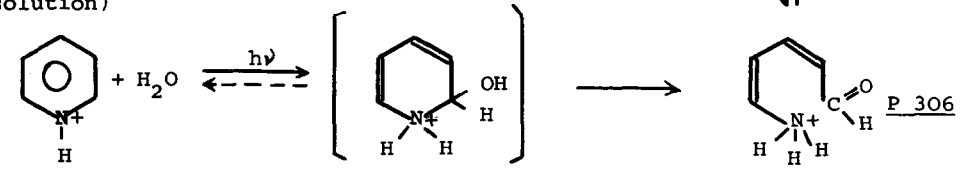
Photoproduct P 360 gives a silver precipitate with TOLLENS's reagent, reduces FEHLING's solution and gives a crystalline phenylhydrazone.

We suggest the following mechanism to account for the different reactions observed. Pyridine, under UV irradiation, adds a molecule of water to give an intermediate that leads, after hydrogen migration, to the unsaturated aminoaldehyde which we have called P 360. In basic solution, if the all cis

(in basic solution)



(in acid solution)



configuration is maintained, this product can revert in the dark to pyridine. In acid solution, the electron pair on the nitrogen is shared probably stabilizing the intermediate product, which could be the product that absorbs at 345 nm, and finally giving the acid form P 306. This product can not revert to pyridine since the electron pair necessary for ring closure is shared by a proton.

Acknowledgment is made to Dr. STREITH and Dr. RUBIN for helpful suggestions.

REFERENCES

(1) H. FREYTAG and W. NEUDERT, J. Prakt. Chem. 135, 15 (1932)
H. FREYTAG and F. HLUCKA, J. Prakt. Chem. 135, 288 (1932)
H. FREYTAG J. Prakt. Chem. 139, 44 (1934)