Tetrahedron Letters No.20, pp. 1689-1691, 1970. Pergamon Press. Printed in Great Britain.

PHOTOISOMERIZATION OF p-NITROBENZALDEHYDE[1]

Gene W. Wubbels, Richard R. Hautala and Robert L. Letsinger
Department of Chemistry, Northwestern University
Evanston, Illinois 60201

(Received in USA 24 February 1970; received in UK for publication 31 March 1970)

A rule formulated by Sachs and Hilpert[2] states that aromatic nitro compounds which contain aliphatic C-H ortho to the nitro group are light sensitive. The photoreactions, which include the well-known isomerization of o-nitrobenzaldehyde to o-nitrosobenzoic acids[3,4] and the photochromic transformations of substituted o-nitrotoluenes[5], appear to proceed via six membered cyclic transition states. m-Nitrobenzaldehyde and p-nitrobenzaldehyde are reported to be relatively stabile, failing to isomerize (though slowly yielding other products) when irradiated in ethanol[3], methanol[6], ether[6], toluene[6], benzene[7], or in the solid state[7]. We now wish to report that the photoinduced isomerization is more general than heretofore recognized and proceeds smoothly in an aqueous medium even when nitro and aldehyde groups are in para positions.

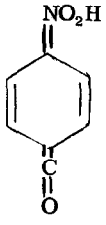
Preliminary experiments showed that p-nitrobenzaldehyde (1.0×10^{-4}M) reacted readily when irradiated under nitrogen in distilled water at 25° with light in the range of 290-400 nm. The maximun in the uv spectrum at 267 nm disappeared and new maxima developed at 287 and 308 nm with an isosbestic point at 282 nm. The final spectrum agreed well with that for p-nitrosobenzoic acid. Neither oxygen nor iodide ion (10^{-2}M) had a noticeable effect on the efficiency of the reaction. Under the same conditions of irradiation m-nitrobenzaldehyde was essentially unchanged. In the isomerization of p-nitrobenzaldehyde the solvent plays a critical role. No change was observed when p-nitrobenzaldehyde was irradiated in hexane for periods longer than required for complete reaction in water. p-Nitrobenzaldehyde reacted slowly when irradiated in methanol or ethyl ether; however, the spectral changes were complex(no isosbestic point) and indicated that the reaction followed a path different from that in water.

For isolation of the product, 50 mg (0.33mmol)of p-nitrobenzaldehyde in one liter of doubly distilled water was irradiated through a Vycor filter sleeve with a 250 w Hanovia lamp for two hours. The solvent was evaporated in vacuo at 35-40° and the residue was dried by distillation of benzene and then taken up in methanol. Concentration of the

methanol extract afforded 40 mg (80%) of p-nitrosobenzoic acid, identified by comparison of its decomposition point (260°, turned brown; lit[8] 250°) and infrared spectrum with values for a sample of p-nitrosobenzoic acid prepared independently. In another experiment the irradiation products were extracted with ethyl acetate from the aqueous solution and, after evaporation of the organic solvent, were heated with excess methanol in the presence of a trace of hydrochloric acid to effect esterification. Concentration of the solution and analysis by gas chromatography showed a single product peak, and this peak was enhanced when authentic methyl p-nitrosobenzoate was added to the solution.

The quantum yield for conversion of p-nitrobenzaldehyde to p-nitrosobenzoic acid at 25° was found to be 0.037 (for this measurement the aqueous solution was irradiated with light from a Bausch and Lomb monochromator set at 270 nm and the extent of reaction was determined from the change in absorbance at 270 nm). This reaction is therefore considerably less efficient than the photoisomerization of o-nitrobenzaldehyde, for which quantum yields of about 0.5 in a variety of solvents have been reported[4].

An attractive intermediate for the isomerization is represented by III. This intermediate, which could form by stepwise transfer (possibly assisted by water molecules) of a hydrogen atom from the aldehyde group to the nitro group, could revert to the aldehyde or, in the presence of water, afford p-nitrosobenzoic acid by addition and loss of the elements of water. The stability of m-nitrobenzaldehyde to irradiation in water may stem from the inability of the meta isomer to form a conjugated intermediate of this type.



III

REFERENCES

1. Photoinduced Substitution IX. Part VIII K. E. Steller and R. L. Letsinger, J. Org. Chem., in press. This research was supported by the National Science Foundation.
2. F. Sachs and S. Hilpert, Chem. Ber., 37, 3425 (1904).
3. G. Ciamician and P. Silber, ibid., 34, 2040 (1901).
4. J. G. Calvert and J. N. Pitts, Jr., "Photochemistry", John Wiley and Sons, Inc., New York, N. Y., 1966, p 479 and references therein.
5. R. Exelby and R. Grinter, Chem. Rev., 65, 247 (1965).
6. E. Bamberger and F. Elger, Ann. Chem., 475, 288 (1929).
7. A. Kailan, Montash. Chem., 33, 1305 (1912).
8. F. J. Alway, Amer. Chem. J., 32, 385 (1904).