

DIMER FORMATION IN THE PHOTOLYSIS OF DIACETYLANHYDROURIDINE IN AQUEOUS SOLUTION\*

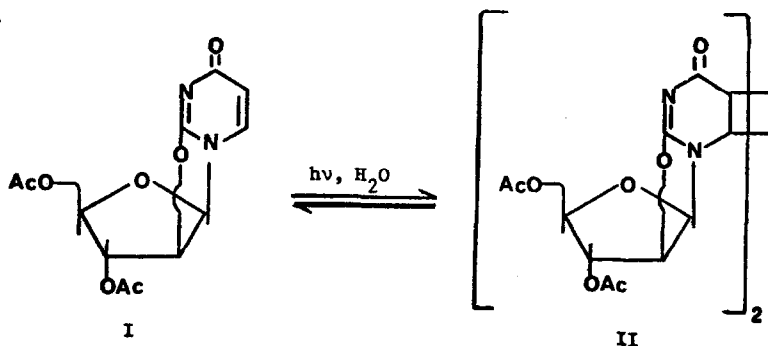
Kelvin K. Ogilvie and John W. Berestiansky

Department of Chemistry, University of Manitoba,

Winnipeg, Manitoba, Canada.

(Received in USA 7 September 1972; received in UK for publication 10 October 1972)

Anhydronucleosides are important analogues of natural nucleosides (1,2) and have recently been incorporated into nucleotide chains (3,4). Because of this and the possibility that these cyclonucleosides may have been intermediates in prebiotic photoinduced formation of polynucleotides (5), we wish to report on the photodimerization of 0<sup>3'</sup>,0<sup>5'</sup>-diacetyl-0<sup>2</sup>,2'-anhydrouridine (I) in aqueous solution.



Irradiation of an aqueous solution of I (1 mg/ml) in a quartz vessel using a low pressure mercury lamp led to a photostationary state consisting of I and its dimer II. Dimer II was isolated by paper chromatography (5%,  $R_f$  0.38 in *n*-butanol-water-ethanol, 4:5:1, Whatman 3MM paper); mp 148-149°C;  $\lambda_{\text{max}}^{\text{H}_2\text{O}}$  241 nm ( $\epsilon$  1.54 x 10<sup>4</sup>),  $\lambda_{\text{min}}^{\text{H}_2\text{O}}$  218 nm ( $\epsilon$  3.65 x 10<sup>3</sup>); anal. (6) calc'd for C<sub>26</sub>H<sub>28</sub>O<sub>14</sub>N<sub>4</sub> · H<sub>2</sub>O: C, 47.56; H, 4.91; N, 8.53. Found: C, 47.60; H, 4.56; N, 8.41; molecular weight (6): calc'd for II:620. Found: 605; the infrared spectrum (KBr disk) of II is completely different from I showing major peaks at 1750, 1600, 1480, 1370, 1235 and 1159 cm<sup>-1</sup>, the band at 1640 cm<sup>-1</sup> characteristic of anhydrouridines was no longer present.

The mass spectrum of II showed a parent peak of 310 and a fragmentation pattern similar to I. This is characteristic of the photodimers of pyrimidine nucleosides which monomerize on electron impact (7).

Photolysis of dilute (10<sup>-4</sup> M) aqueous solutions of II at 254 nm quantitatively converted II to its monomer I. Again this is behavior typical of photodimers of the pyrimidine nucleosides (7).

Irradiation of aqueous solutions of I through a pyrex filter had no effect on I. However, using acetone as a sensitizer I was converted to II using a pyrex filter which again parallels the photochemistry of the natural pyrimidines (8).

This research was supported by the National Research Council of Canada. We gratefully acknowledge numerous helpful discussions with Dr. J.L. Charlton.

\*Part X in a series on anhydronucleosides.

1. J.J. Fox, *Pure and Applied Chemistry*, 18, 223 (1969).
2. M. Ikehara, *Accts. Chem. Res.*, 2, 47 (1969).
3. S. Uesugi, M. Yasumoto, M. Ikehara, K. Fang, P.O.P. Ts'O, *J. Am. Chem. Soc.*, 94, 5480 (1972).
4. K.K. Ogilvie and D. Iwacha, *Can. J. Chem.*, 48, 862 (1970).
5. J. Nagyvary and K.L. Nagpal, *Science*, 177, 272 (1972).
6. Performed by Galbraith Labs. Inc., Knoxville, Tenn.
7. J.G. Burr in *Advances in Photochemistry*, 6, p. 193 (1968), Interscience, New York.
8. I. Rosenthal and D. Elad, *Photochem. and Photobiol.*, 8, 145 (1968).