

A PHOTOCHEMICAL REARRANGEMENT OF 5-CYCLOPROPYLURACIL

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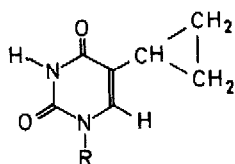
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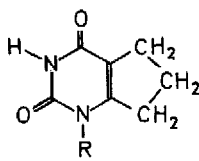
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We wish to report herein the photochemical behaviour of 5-cyclopropyluracil¹ (I) and 5-cyclopropyluridine² (II).



I ; R = H
II ; R = β -D-ribofuranosyl



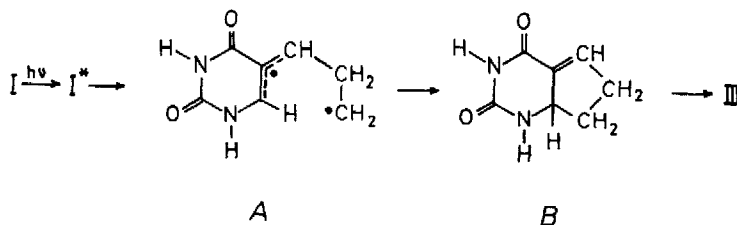
III ; R = H
IV ; R = β -D-ribofuranosyl

Irradiation³ of an aqueous 10^{-3} M solution of I with a low-pressure mercury lamp up to complete conversion (30 min) resulted in the formation of the only UV absorbing product (in 80% yield) which was identified spectroscopically (UV, ¹H-NMR) as 5,6-trimethyleneturacil⁴ (III). The photochemical behaviour of I is in a contrast to that of 5-alkyluracils which undergo the photochemical dealkylation.⁵

The rearrangement of I into III may be rationalized as a three-step process involving the formation of diradical intermediate A, its stabilisation by ring closure to B, and the proton transfer to III (Scheme 1). The formation of the diradical species A seems to be favoured by the enhanced uncoupled electron density on C-5 and C-6 in the excited state of I. This assumption was made on the base of the MO calculations pertaining to the first excited state of uracil and thymine.⁶ The radical fission of the cyclopropane ring might be facilitated by the excited state overlap of the MO of the $\tilde{\pi}$ -system with that of the cyclopropane ring. This effect has been considered as significant⁷ in controlling the course of cyclopropane ring cleavage in photochemical reactions of cyclopropyl ketones and arylcyclopropanes. The diminished photoisomerisation rate of 5-cyclopropyl-2-thiouracil, the rate constant of which is five times lower than that of compound I, may be due to a lower spin density on C-5 and C-6 in the excited state of 5-cyclopropyl-2-

-thiouracil. This electron distribution can be inferred from the MO calculations obtained for 2-thiouracil.⁶

The readiness of the photochemical isomerisation of I to III prompted us to extend our investigation to the nucleoside II. When compound II was irradiated for 20 min under conditions stated above, no starting material was detected and the major UV absorbing product (in 60% yield) was identified as 5,6-trimethyleneuridine (IV) by comparing its TLC mobility and UV spectra with those of an authentic sample.⁸ For rigorous structural proof, the crude photoproduct was acetylated and the acetate (after chromatographical purification) identified as 2',3',5'-tri-O-acetyl-5,6-trimethyleneuridine by the superimposed ¹H-NMR spectrum with that of an authentic specimen.⁸



Scheme 1

The smoothly proceeding photochemical rearrangement of II to IV offers an opportunity to investigate the anti/syn conformational change of a nucleotide unit in modified RNA's and DNA's provided that the incorporation of I into the biopolymers would be feasible.

References and Notes

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3. Irradiation was performed on a merry-go-round apparatus equipped with sixteen 5 W-low-pressure mercury lamps. A quartz photoreactor was surrounded by a liquid filter (33% aqueous sodium acetate solution in the layer thick of 0.5 cm). The temperature was kept below 30°C by an immersion cooler. The reaction mixture was stirred by a stream of nitrogen. The light output on the surface of the irradiated solution was 3.3×10^{-7} Einstein \cdot cm⁻² min⁻¹. The actinometry was based on the measurement of photohydration of uridine.⁹
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