

NOTE

pH Dependent Photo transformation of Some Pyrimidines: Part II

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When some pyrimidines, *viz.*, thymine, uracil and cytosine were irradiated by UV light in alkaline medium, they underwent photo transformation giving various products which have been characterized by spectral data and elemental analysis. Thymine undergoes ring expansion by the insertion of $-\text{CH}_3$ group whereas uracil and cytosine gives photodimers.

Photochemistry of pyrimidines has been studied extensively^{1–20}. Most of these studies have been carried out on nucleic acids. In continuation of our studies on the effect of pH on the course of photochemical reaction^{21, 22}, here we report the phototransformation of some free pyrimidines in alkaline medium.

The pyrimidines (2 g) were dissolved in distilled water (200 mL). The solution was made alkaline by adding 0.5 mL of 10% NaOH solution. Benzophenone was added as sensitizer. The solution was then irradiated by 125 W mercury vapour lamp. The progress of the reaction was observed by TLC in butanol : acetic acid : water (12 : 3 : 5 v/v) solvent system. After the completion of the reaction, the solution was neutralized, concentrated and then placed in the fridge overnight. Colourless crystals were obtained which were filtered, washed with water and recrystallized from ethanol.

The m.p., yields and the elemental analysis data of the products II, IV and VI are given in Table-1.

TABLE-1

Product	m.p. (°C)	Yield (g)	Found (%)	Calcd. (%)
II	306–308	0.6	C 47.84, H. 4.51, N 22.53	$\text{C}_5\text{H}_5\text{N}_2\text{O}_2$ requires C 47.62, H 4.76, N 22.22
IV	302–303	0.5	C 42.54, H. 3.35, N 24.82	$\text{C}_8\text{H}_8\text{N}_4\text{O}_4$ requires C 42.86, H 3.57, N 25.00
VI	340–342	0.8	C 46.06, H. 4.66, N 37.76	$\text{C}_8\text{H}_{10}\text{N}_6\text{O}_2$ requires C 43.20, H 4.50, N 37.84

Thymine (I), when irradiated by UV light in alkaline medium, underwent ring expansion by the insertion of $-\text{CH}_3$ group, giving the product (II). The IR spectrum (KBr) of II gives absorptions at (cm^{-1}): 3200 (N—H stretch), 3060 ($=\text{CH}$ stretch), 2930 ($> \text{CH}_2$ stretch), 1730 (C=O stretch), 1670 (C=N stretch),

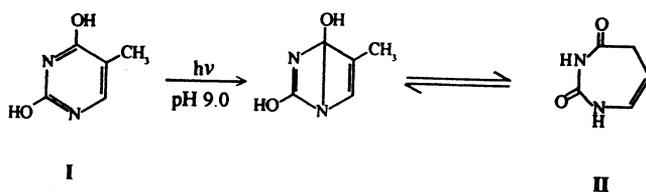


Fig. 1

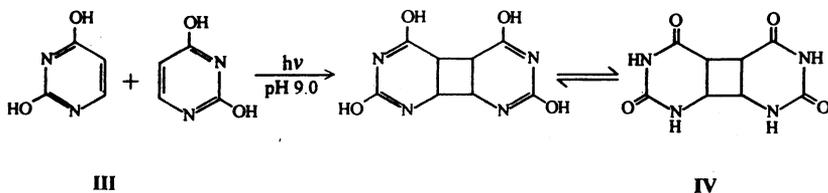


Fig. 2

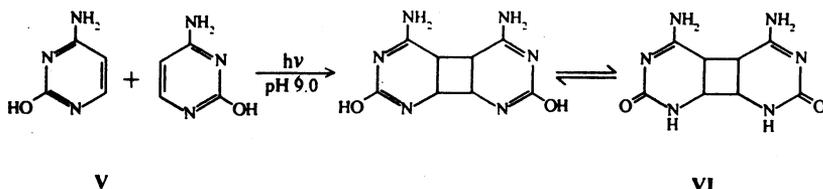


Fig. 3

1620 (C=C stretch). Its $^1\text{H NMR}$ (90 MHz, DMSO-d_6) gives signals at δ 8.8 (d, $J = 5$ Hz, NCH = proton), 8.4 (m, =CH protons), 8 (s, NH proton) and 2.9 (d, $J = 4$ Hz, $>\text{CH}_2$ protons). The mass spectrum gives the M^+ peak at m/z 126, corresponding to the molecular weight of **II** and a $\text{M} + 1$ peak at m/z 127, indicating the presence of nitrogen. Other important peaks are observed at m/z 125 ($\text{M}^+ - \text{H}$), 83 ($\text{M}^+ - \text{NHCO}$), 55 ($83 - \text{CO}$) etc.

Uracil (**III**) and cytosine (**V**), both undergo dimerization giving the products **IV** and **VI** respectively upon irradiation by UV light in alkaline medium. IR spectrum (KBr) of **IV** shows important peaks at (cm^{-1}): 3100 (N—H stretch), 2920 (C—H stretch, alicyclic), 1715 (C=O stretch), 1655 (C=N stretch), 1640 (C=C stretch), 960 (cyclobutane ring)¹. Its $^1\text{H NMR}$ (90 MHz, DMSO-d_6) shows absorptions at δ 3.8 and 4.10 (s, cyclobutane protons)³ and 8.0 (s, NH protons). Its mass spectrum does not give the molecular ion peak, but gives the base peak at m/z 112, corresponding to the molecular weight of the monomer, indicating

that the molecule dissociates into monomer under the conditions used in the instrument. Other important peaks are observed at m/z 113 ($M + 1$, due to nitrogen), 95 ($M^+ - OH$), 84 ($M^+ - CO$), 69 ($M^+ - NHCO$), 42 (69—HCN) etc.

The dimer VI, in its IR spectrum, gives important peaks at (cm^{-1}) 3350 (N—H stretch), 2930 (C—H stretch), alicyclic), 1700 (C=O stretch), 1500 (N—H bending), 965 (Cyclobutane ring)¹ etc. Its ¹H NMR (90 MHz, DMSO- d_6) gives peaks at δ 7.4 (s, NH₂ protons), 5.7 (s, NH protons) and 4.3 (s, cyclobutane protons)³. Its mass spectrum gives very weak molecular ion peak at m/z 222; the base peak is at m/z 111 corresponding to the molecular weight of the monomer; other important peaks are at m/z 97 (111—NH₂), 83 (111—CO), 56 (83—HCN) etc.

The *cis-syn*, head-to-head stereochemistry of the dimers has been proposed on the basis of the literature reports.^{3, 15-17} Many workers have studied the photo dimerization of thymine under different conditions and have reported the formation of *cis-syn*, head-to-head dimer as the major product.^{3, 15-17} Merriam and Godon²⁰ have also reported *cis-syn*, head-to-head dimer of uracil from irradiated DNA.

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