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Photolysis of Some Pyrimidines by UV Light: Part I

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Pyrimidines, *viz.*, thymine, cytosine and uracil when photolysed by UV light, gave the dimer (II) and dewar-2-pyrimidones (IV) and (VI) respectively. The structures of these products have been established by spectral and elemental analysis.

INTRODUCTION

Photochemistry of pyrimidines has been extensively studied. All these reactions have been carried out under different conditions[1–17]. In the present paper we report the photochemical reaction of some pyrimidines in acidic medium.

EXPERIMENTAL

(i) Reaction of thymine in acidic medium: Thymine (3 g) was dissolved in double distilled water (200 mL) in a double walled glass beaker. To this solution 2 mL of dilute HCl was added. The pH was recorded on a digital pH meter and 2 g benzophenone was added as sensitizer and then the solution was irradiated by a 125 W mercury arc lamp.

The reaction completed in 40 h and then the irradiation was stopped. The reaction mixture was neutralised and concentrated by distillation on a water bath under reduced pressure and was placed at room temperature overnight. The colourless crystals were obtained which were filtered and recrystallised from ethanol to give colourless needles, m.p. 302–304°C, yield 1.4 g. Found: C 47.80, N 21.95 and H 4.66%. $C_{10}H_{12}N_4O_4$ requires C 47.62, N 22.22 and H 4.76%.

(ii) Reaction of cytosine in acidic medium: Cytosine was dissolved in double distilled water and ethanol (1 : 1, 300 mL). The reaction was carried out in the same manner as in the previous experiment. The reaction completed in 44 h. The product obtained was recrystallised twice with benzene, m.p. 303–305°C, yield 1.8 g. Found: C 43.10, N 37.99 and H 4.40%. $C_4H_5N_3O$ requires C 43.24, N 37.84 and H 4.50%.

(iii) Reaction of uracil in acidic medium: Uracil was dissolved in double distilled water and acetone (1 : 1, 200 mL). The reaction was carried out in the same manner as in the previous experiment. The reaction completed in 32 h. The product obtained was recrystallized from C_2H_5OH, m.p. 29–30°C, yield 1.6 g. Found: C 42.36, N 24.70 and H 3.18%. $C_4H_4N_2O_2$ requires C 42.86, N 25.00 and H 3.57%.

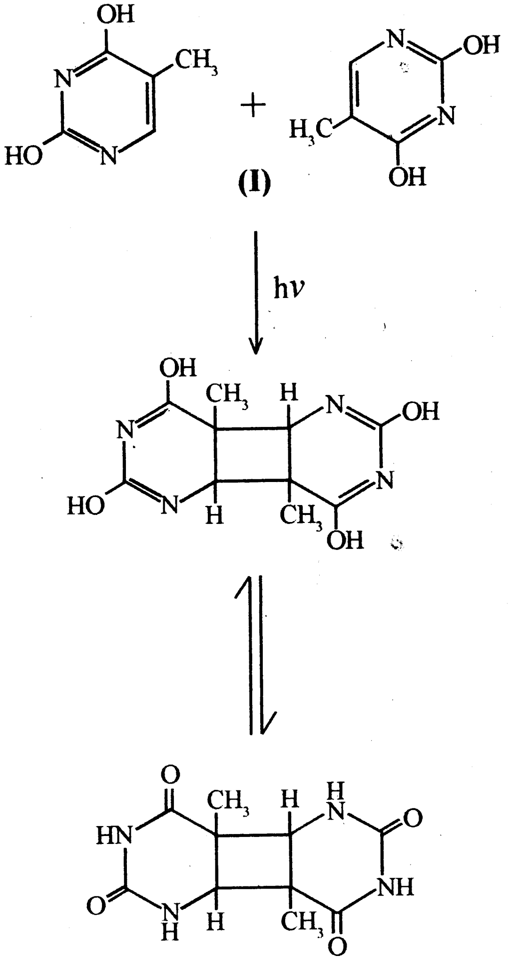
(i) Reaction of thymine: When thymine (I) was irradiated by UV light, it gave a dimer **(II)** (Fig. 1). The same dimer has been reported by Beukers and Berends[1] by the irradiation of thymine in frozen aqueous solution.

The ^{1}H NMR spectrum of the dimer shows an absorption peak at δ 1.7 (—CH_3 proton) and at δ 7.2 (ring junction proton).

Its IR spectrum shows a weak peak at 960 cm^{-1}, showing a cyclobutane ring system along with the other peaks.

The mass spectrum gives the molecular ion peak at m/e 126, showing that the product dissociates into thymine under the conditions used in the apparatus.

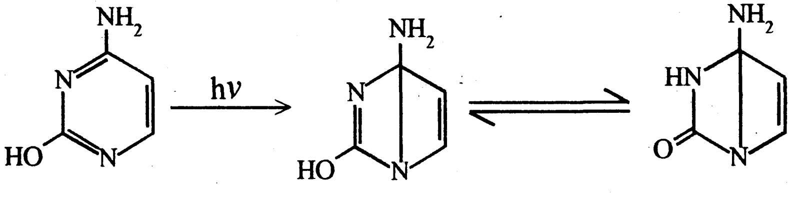
The same spectral data was reported by Beukers and Berends[1].



(II)

Fig. 1

(ii) Reaction of cytosine: On irradiation the cytosine **(III)** gave Dewar type compound **(IV)** (Fig. 2).



(III) **(IV)**

Fig. 2

The structure of the product **(IV)** was confirmed by spectral data and elemental analysis.

The IR spectrum of the product shows carbonyl absorption at 1730 cm^{-1}, broad band at 3310 and 3100 cm^{-1} (—NH and —OH stretching), 1700 cm^{-1} (C═N stretching), 1650 cm^{-1} (C═C stretching), 1570, 1540 cm^{-1} (—NH bending), etc.

The cytosine shows carbonyl absorption at 1690 cm^{-1} as a broad band (because it is tautomeric) and the product shows carbonyl absorption at 1730 cm^{-1} indicating the loss of conjugation.

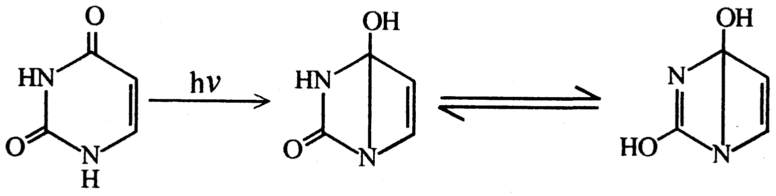
The UV absorption spectrum of the product shows carbonyl absorption at 240 nm.

The ^1H NMR spectrum of product shows peaks at δ 6.15 (—CH protons), δ 7.8 (NH_2 protons) and δ 8.8 (—OH protons).

The mass spectrum gives the molecular ion peak at m/e 111, which is also the base peak, corresponding to the molecular weight of the product. The spectrum also shows a M + 1 peak at m/e 112 indicating the presence of N.

Same type of products have also been reported in the photochemical reaction of 4-pyrimidones by Takao Yamazaki[10].

(iii) Reaction of Uracil: On irradiation uracil **(V)** also gave the Dewar type compound **(VI)** (Fig. 3).

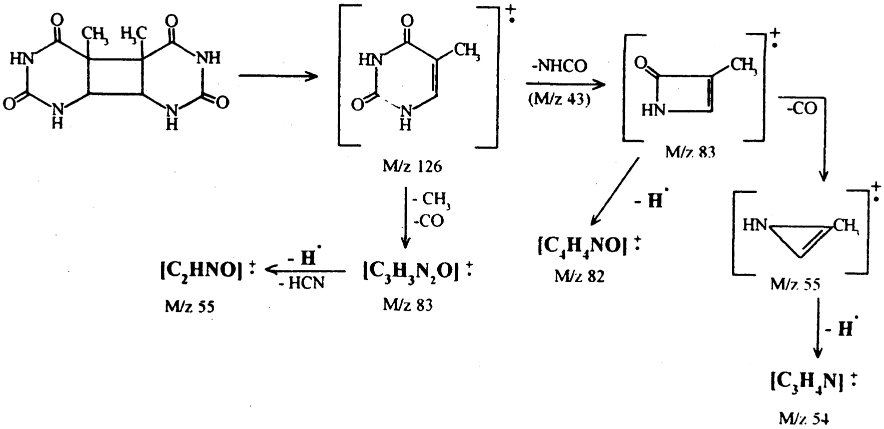


(V) **(VI)**

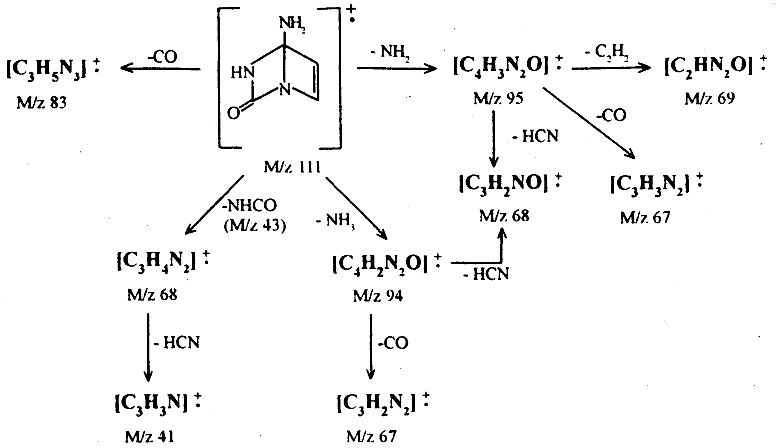
Fig. 3

The structure of the product **(VI)** was confirmed by spectral data and elemental analysis.

The IR spectrum of the product shows peaks at 3110 cm^{-1} (O—H stretching),



Scheme 1



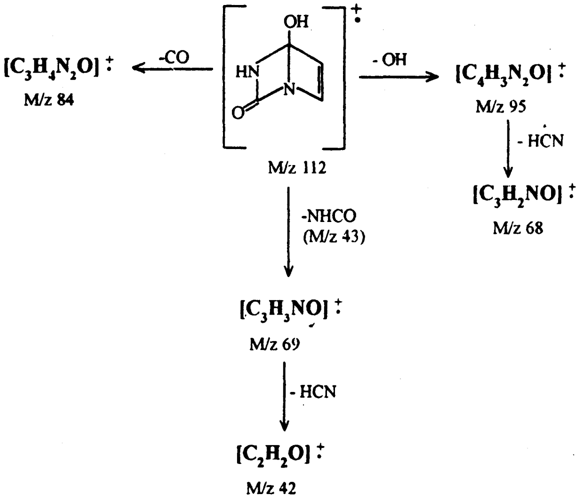
Scheme 2

1725 cm^{-1} (C═O stretching), 1650 cm^{-1} (C═C stretching), 1510 cm^{-1} (N—N bending), 1395, 1010 cm^{-1}, etc.

The ^{1}H NMR spectrum of the product shows peaks at δ 5.4 (CH protons) and δ 7.4 (OH protons).

The UV absorption spectrum of the product shows C═O absorption at 240 nm.

The mass spectrum of the product shows the molecular ion peak which is also the base peak at m/e 112 corresponding to the molecular weight of the compound. A M + 1 peak at m/e 113 indicates the presence of nitrogen.



Scheme 3

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