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STEROID PHOTOCHEMISTRY: PHOTOCHEMICAL REACTION OF 3β-ACETOXY-16,17-SECO- Δ^5-ANDROSTEN-16,17-IMIDE

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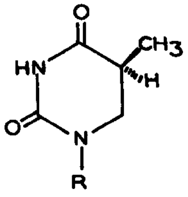
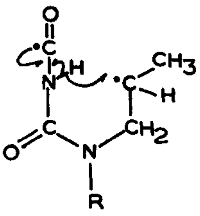
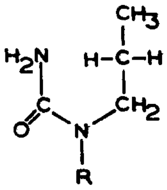
Witkop (1) has recently reported that dihydrothymidine (I) undergoes Ciamician-Silber type photohydrolysis to the urea derivative (II) and that the change I →II involves an intramolecular hydrogen transfer through a six-membered transition state (A).



I



[A]



II

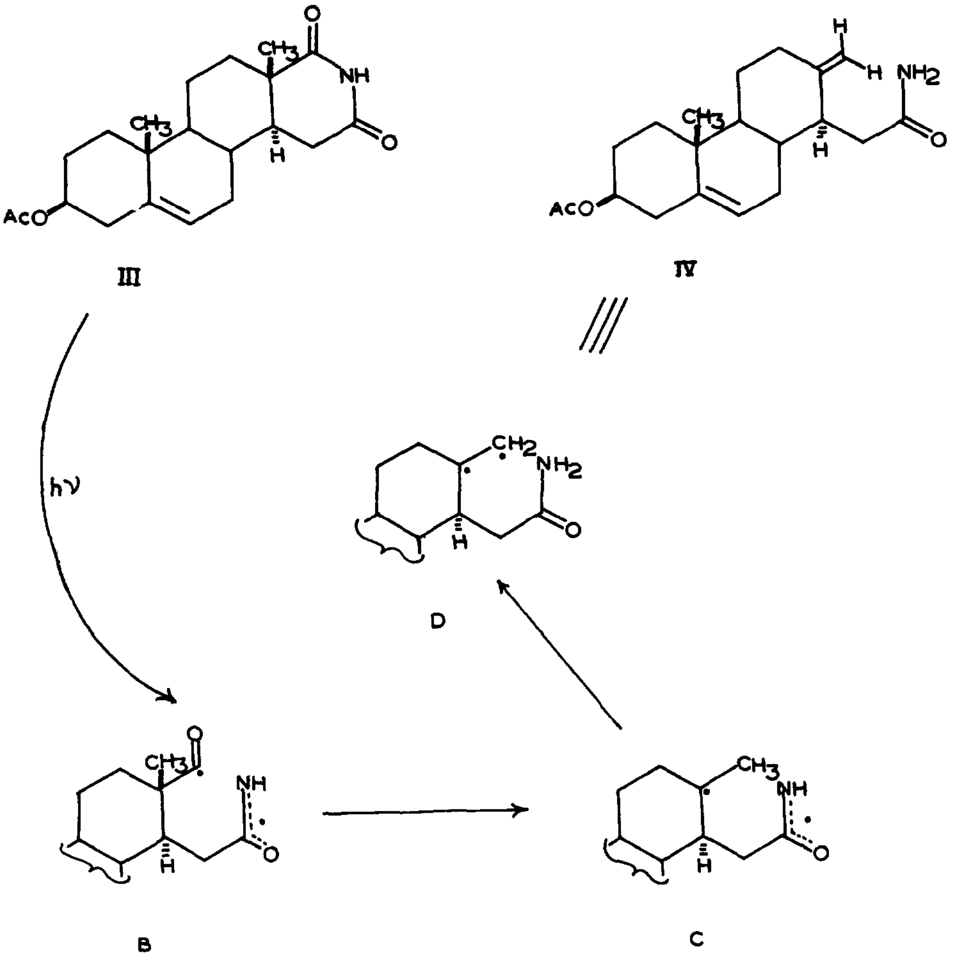
R=H, deoxyribose

Further to our work on the photolysis of steroidal lactams possessing unsaturation in the vicinity of the lactam moiety (2), we have studied the photochemical behaviour of 3β-acetoxy-16,17-seco- Δ^5-androsten-16,17-imide (III) and report herein an interesting observation (3).

Irradiation of 0.7 g of III (4) in THF for a total of 48 hrs gave, after chromatography (silica gel; benzene-ethyl acetate, 23:2), 0.15 g of IV, mp 193-94°, besides the unaffected (III) and an intractable oil (5). The structure of IV is brought out completely from its various spectra. Its mass spectrum (m/e 331,M^+, 24% of the base peak at m/e 197) exhibited loss of 28 mass units (CO) in the transformation III → IV. Its solid phase IR spectrum (nujol) revealed it to be a primary amide (ν_{max} 1640 cm^{-1}, amide band II; 1625 cm^{-1}, amide band I; 3395 and 3210 cm^{-1}, N-H) (6) confirmed by the observation of a broad two-proton signal in its NMR between δ 6.00-5.80 (NH_2) (7); in III, the imidic H appeared as a broad singlet around δ 8.48. Further, the NMR spectrum of IV showed only one t-methyl singlet at δ 0.94 suggesting obviously participation of C_{13}-methyl (in III, δ 1.23) during its conversion into IV(8). The fate of this methyl became known with the observation of two little singlets (in IV) located respectively at δ 4.80 ($w^{\frac{1}{2}}$ 4 Hz) and δ 4.67 ($w^{\frac{1}{2}}$ 4 Hz) indicative of two terminal olefinic hydrogens having a small geminal coupling between them (cf. 9).

Presumably, the phototransformation III → IV involves interception by a seven-membered cyclic transition state in an intramolecular hydrogen transfer (C → D, mechanistic scheme) though the loss of CO in the solution phase photolysis of the amide is unexceptional (10).

Our preference for the initial CO-NH bond cleavage in III (leading to diradical B) is based purely on our experience with other amides (2) although there is nothing to exclude role of the diradical resulting from initial C_{13}-CO bond fission.



References and Footnotes

1. Y. Kondo and B. Witkop, J. Am. Chem. Soc., 90, 3258 (1968).

2. R.P. Gandhi, Majar Singh, Y.P. Sachdeva and S.M. Mukherji, Tet. Lett., Preceding communication.

3. Abstracted in part from Ph.D. dissertation of Majar Singh, Kurukshetra University, India, 1971.

4. Made according to B.M. Regan and F.N. Hayes, J. Am. Chem. Soc., 78, 639 (1956). The structure of III was checked through its NMR and mass spectra.

5. Photolysis was carried out with a 250 watts medium pressure mercury lamp in a quartz vessel using nitrogen atmosphere.

6. C.N.R. Rao, 'Chemical Applications of IR spectroscopy', Academic Press, London, 1963, p. 258.

7. The 6-olefinic H multiplet in IV showed up at δ 5.50 - 5.32.

8. NMR and mass spectra were recorded respectively on a Varian A-60-D machine (on $CDCl_3$ solutions) and a CEC model 21-110B spectrometer.

9. N.S. Bhacca and D.H. Williams, 'Applications of NMR spectroscopy to Organic Chemistry', Holden-Day, 1964, p. 57.

10. C.H. Nicholls and P.A. Leermakers, J. Org. Chem., 35, 2754 (1970).