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# PHOTOCHEMICAL REORGANISATION IN
# 4-PHENYL-$\Delta^5$-4-AZA-3-OXO-STEROIDS

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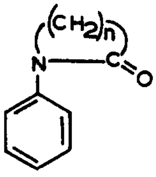
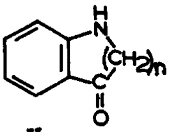
Recently, Fischer (1) described the photochemical conversion of N-phenyl-lactam (I) into the ketone (II). Hoffmann (2) and Yang (3) reported that the acyclic enamides undergo intramolecular photochemical rearrangement, through acyl migration, to vinylogous amides. Horii (4), however, has found that the cyclic enamide (III), upon irradiation in methanol or amines, produces the oxo-carboxylic acid derivatives (IV) presumably through a ketene intermediate.


I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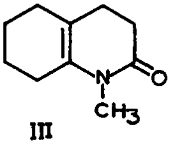
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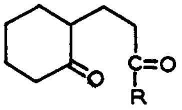
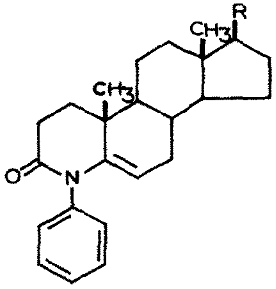

IV R= OMe, NHR'

We now wish to report that the photolysis of 4-phenyl-$\Delta^5$-4-azacholesten-3-one (Va) (an enamide possessing an N-phenyl substitution) produces an interesting ring A enlargement in Va leading to VIa by an intramolecular rearrangement (5).

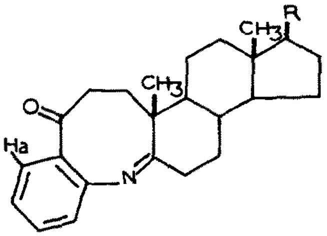
Irradiation of a solution of 2.2 g of Va in dioxane for 72 hrs followed by chromatography (silica gel; benzene) gave 0.35 g of VIa, mp 205$^{\circ}$ (6). Its structure followed from the considerations of its mass spectrometric mol. wt. (461), and its UV spectrum ($\lambda^{\text{ethanol}}_{\text{max}}$ 248 mμ) revealing the presence of an aromatically conjugated ketone confirmed by a strong band in the IR at 1665 cm$^{-1}$. The IR spectrum further revealed, through a band of medium intensity at 1605 cm$^{-1}$, a C=N (exhibiting greater polar character); no other bands were present in the functional group region of its IR. In the region of significance in its NMR spectrum (which showed absence of any olefinic proton), the integral trace of the aromatic resonances indicated four such protons one of which (Ha, multiplet around $\delta$ 7.76, spacing between end lines, 10.2 Hz) is shifted well below the main cluster of other aromatic resonances (3H, $\delta$ 7.32 - 6.93) (7).

A similar photolysis (8) of 4-phenyl-$\Delta^{5}$-4-aza-androsten-3-one-17β-ol-17-acetate (Vb; 2 g) (9) in THF furnished, after chromatography (silica gel; benzene - ethyl acetate, 19:1), 0.15 g of VIb, mp 200$^{\circ}$: m/e 407 ($M^{+}$, base peak); $\nu^{\text{nujol}}_{\text{max}}$ 1670-1660 (s, conj. C=O), 1610 (m-w, C=N), 1745 (OCOCH$_3$) cm$^{-1}$; NMR, region of interest, multiplet around $\delta$ 7.85 (1 Aromatic H, spacing between end lines, 12.2 Hz, Ha), $\delta$ 7.43 - 7.03 (3 Aromatic H, multiplet), $\delta$ 4.82 - 4.60 (1H, multiplet, 17αH), $\delta$ 2.07 (OCOCH$_3$); no olefinic H (10).

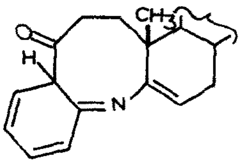
It is of interest to mention here that the mass spectra of VIa and VIb, though weak in general, each reveal the formation of ions of mass 198 (resulting from the facile loss of rings C/D as in A) which are next in abundance only to the respective molecular ions (m/e 198: VIa, Rel. Int. 15; VIb, Rel. Int. 38).



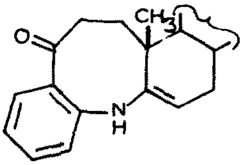
V



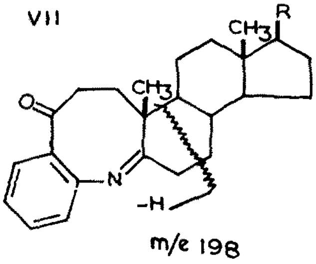
VI



VII



VIII



A

a) R= $C_8H_{17}$

b) R= OAc

The conversion V → VI presumably involves interception by VII, which may go to VI via amine VIII.

## References and Footnotes

1. M. Fischer, Tet. Lett., 4295 (1968); 2281 (1969).
2. R.W. Hoffmann and K.R. Eichen, Tet. Lett., 1759 (1968).
3. N.C. Yang and G.R. Lenz, Tet. Lett., 4897 (1967).
4. Z. Horii, Y. Hori and C. Iwata, Chem. Comm., 1424 (1968).
5. Abstracted in part from the Ph.D. dissertation of Majar Singh, Kurukshetra University, India, 1971.
6. Another compound that came rather later through the chromatogram (benzene-ethyl acetate, 9:1) in minute quantity, had mp. 152°. This will be described in a full paper.
7. Irradiation of Va in ethanol produced the same compounds (VIa, major) though the reaction was somewhat slower.
8. The photolyses were carried out with a 250 watts medium pressure mercury arc using a quartz glass reactor and in nitrogen atmosphere.
9. Vb was made from 5-oxo-3,5-seco-A-nor-androstan-3-oic-acid-17$\beta$-ol, 17-acetate and aniline, and its structure was confirmed through its mass, IR and NMR spectra.
10. NMR spectra were taken on a Varian A-60-D machine in $CDCl_3/CCl_4$ and the mass spectra were recorded at 70 ev on a CEC (model 21-110B) mass spectrometer.