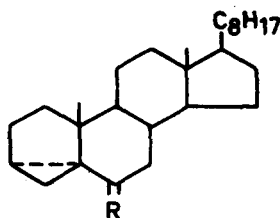


**ATTEMPTED ACID-CATALYSED HYDROLYSIS OF 6-AZA-3 $\alpha$ ,5 $\alpha$ -CYCLO-B-HOMOCHOLESTAN-7-ONE. EVIDENCE FOR RETRO-BECKMANN REARRANGEMENT**

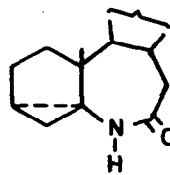
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The lactam, 6-aza-3 $\alpha$ ,5 $\alpha$ -cyclo-B-homocholestan-7-one (II), m.p. 200°;  $[\alpha]_D^{21} + 70^\circ$ , was prepared from the oxime tosylate (I) following the procedure of Craig and Naik<sup>1</sup>. The structure of the lactam (II) was supported by spectral properties\*. The i.r. spectrum of the lactam showed peaks at 3200, 3080(NH), 3036(w) ( $\text{CH}_2$ )<sup>2</sup>, 1670(s), 1658(sh) cm<sup>-1</sup> (CONH). The n.m.r. spectrum (100 M.c.) exhibited signals at  $\delta$  6.88s (-NH-CO-), exchangeable with deuterium<sup>3</sup>. The sharpness of the peak clearly indicated the absence of vicinal proton/s about the -NH group, such as in (II). The absence of vinylic protons and the presence of complex signals in the region  $\delta$  0.4 to 0.68 supported the presence of a cyclopropane system<sup>4</sup> in the lactam (II). Further, the C7 $\alpha$ -protons (methylene) appeared centred at  $\delta$  2.3.



- (I) R = N-OTs  
(III) R = N-OH  
(IV) R = O



(II)

In an attempt to obtain the corresponding amino acid or products derived from it, the lactam (II) was hydrolysed with HBr(48%) in boiling acetone for 8 hr.

\* All the compounds recorded gave satisfactory analytical and spectral values and in known cases comparison was also made with authentic samples.

The usual work up of the reaction mixture, followed by chromatography (silica gel), gave the oxime (III)<sup>5</sup>, the product of retro-Beckmann rearrangement, the cycloketone (IV)<sup>6</sup> (major product), and 3 $\beta$ -bromo-5 $\alpha$ -cholestan-6-one<sup>7</sup>, an artefact of (IV). It was experimentally realized that the oxime (III) was readily converted to (IV) on warming with HBr in acetone for 1 hr., on prolonged heating the cycloketone (IV) was converted to the bromoketone. Apparently the change involved the sequence (II)  $\rightarrow$  (III)  $\rightarrow$  (IV); the same sequence as one would expect if retro-Beckmann rearrangement and deoxygenation were involved.

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