

PHOTOCHEMICAL SYNTHESIS OF 4 β -19-METHYL-IMINO-5- α -CHOLESTANE

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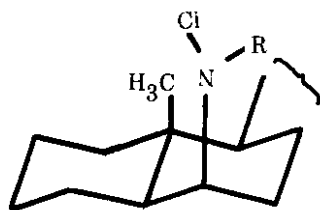
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Summary : Photochemical transformation are outlined with novel stereochemical or other mechanistic features leading to the synthesis of 4 β -19-methyl-imino-5- α -cholestanic.

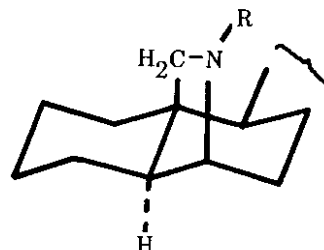
Previously the photochemical cyclisation¹ of the chloramine (1) to 6 β , 19-methyl-imino-5 α -cholestanic (1A) has been reported. We now report the photochemical cyclisation of a strongly sterically hindered chloramine (2), containing the juxtaposition of groups necessary to functionalise the angular non-activated C₍₁₉₎ methyl group by Hoffmann² and Loffler³ reaction to another bridged novel heterocyclic system formulated as 4B, 19-methyl-imino-5 α -cholestanic (2A). It should be pointed out that the use of the strongly sterically hindered chloro amines (1&2) for the synthesis of the novel heterocyclic steroidal bases (1A & 2A) have previously been inhibited^{4,5} inter alia by the instability of 6 β and 4 β chloromethyl amine (1 & 2) arising from syn-axial

compression on the nitrogeneous group by the angular 10-methyl group.

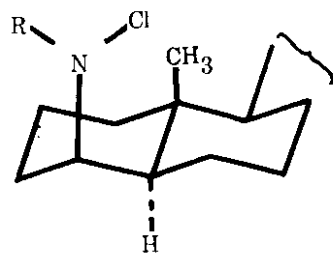
The highly unstable base i.e. 5 α -cholestan-4 β -yl chloromethylamine (2) prepared by treatment of 5 α -cholestan-4 β -ylmethylamine in cyclohexane with hypochlorous acid was stabilized by freeze-drying and subsequently transferred to a quartz tube with freshly distilled trifluoroacetic acid and photolysed at 5 $^{\circ}$ C using a low pressure 450 watt Hanovia lamp in an atmosphere of nitrogen for 8 minutes to afford the base (2A), yield 20%. The mass spectrum showed molecular ion at m/e 399, which was more intense and a metastable peak at 318 was observed which corresponds to $\frac{(356)^2}{(399)} = 317.6$ and can be derived as (3 to 5).



(1)

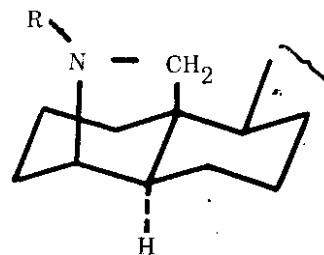


(1-A)



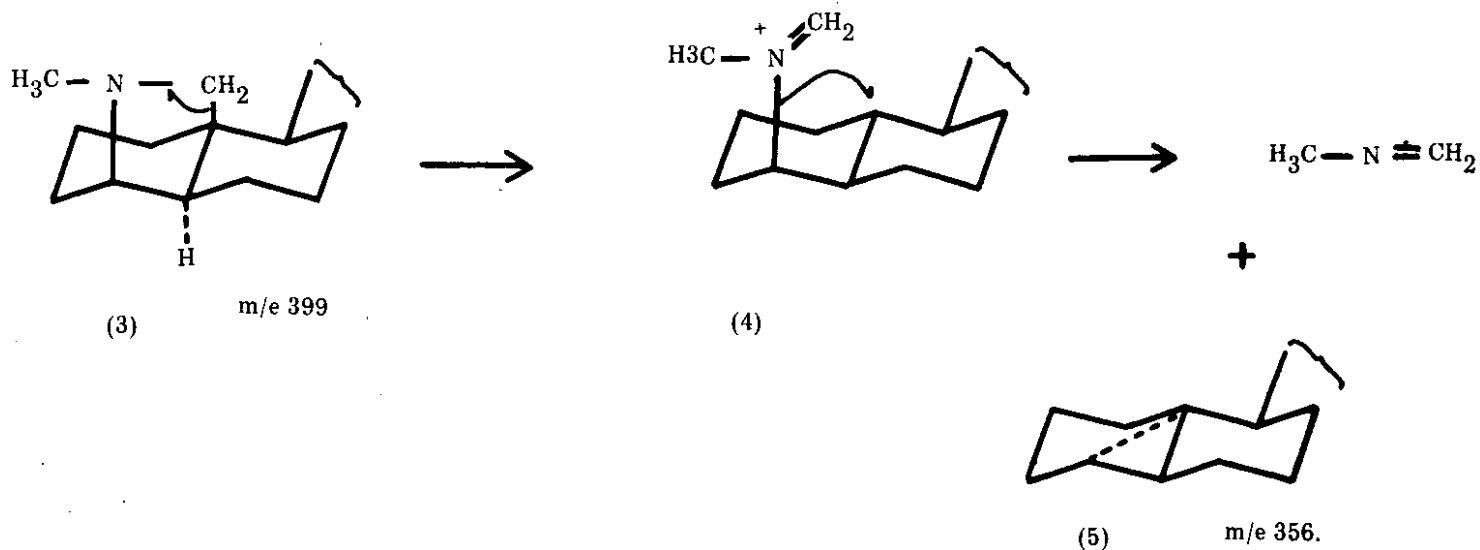
(2)

R=Me



(2-A)

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The methiodide of the base (2A) has m.p. 166-167^o; $[\alpha]_{\text{D}} + 17^{\circ}$; n.m.r. (spectra in CDCl_3), τ 5.65 (1H, broad singlet, 4 α -proton); 6.16 (3H, singlet, N-Me); 6.3 (5H, singlet, N-Me and 19- CH_2 superimposed). Found: C, 64.1; H, 9.6; N, 2.9; I, 23.6%; $\text{C}_{29}\text{H}_{52}\text{NI}$ requires C, 64.3; H, 9.6; N, 2.6; I, 23.5%; mass spectrum m/e 413, (parent peak), metastable peak appeared at 318. In the methiodide of 6 β , 19-imino-5 α -cholestane (1A), the molecular ion appeared m/e 413, but no metastable peak was observed.

Acknowledgements

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References

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5. For a review see Wolff, M.E., *Chem. Rev.*, 63, 55 (1963).