Photolysis of 3β-Acetoxycholest-5-en-19-ol Nitrite

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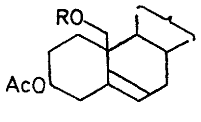
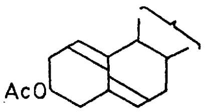
Summary Photolysis of 3β-acetoxycholest-5-en-19-ol nitrite in cyclohexane leads to the elimination of the angular hydroxymethyl group.

Photoreactions of steroidal nitrites have been extensively studied and shown to lead to the formation of oximes by intramolecular exchange of the NO group of the nitrite residue with hydrogen attached to a carbon atom in the γ-position.[1] We examined the photoreaction of the nitrite (Ib) in order to determine the effect of the 5,6-double bond. The cholestenol (Ia)[2] gave the corresponding nitrite (Ib) almost quantitatively on treatment with nitrosyl chloride in pyridine at -20 to $-30°$. Photolysis of (Ib) in cyclohexane in a Pyrex vessel at room temperature under nitrogen using a high-pressure mercury lamp gave on chromatography the diene (II) (7%), m.p. 74—75°, $[\alpha]_D$ $-68°$, M^+ 412, λ_{max} (EtOH) 240 nm (ϵ 14,000), δ ($CDCl_3$) 5·35—5·5 (2H, 6- and 1-H), and the oxime (III) (50%), m.p. 174—175°, $[\alpha]_D$ $+42°$, M^+ 443, λ_{max} (EtOH) 242 nm (ϵ 17,000), ν_{max} (KBr) 3300, 1625, and 735 cm^{-1}, δ ($CDCl_3$) 7·85 (=N–OH), as major products. Photolysis of (Ib) in a glass vessel afforded 20% of (II) and 45% of (III). No significant solvent effect on the product distribution was observed.

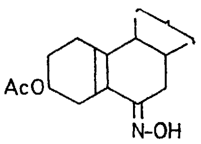
The structures of (II) and (III) were elucidated from spectral data and the following reactions. The n.m.r. spectrum of (II) showed overlapped broad signals due to 1- and 6-H in the olefin region, while that of (III) showed no olefinic proton signal. Catalytic hydrogenation (Pt–HOAc) of (II) led to the consumption of 2 mol. equiv. of hydrogen; the hydrogenation products were identical with those from 3β-acetoxy-19-norcholest-5(10)-ene. Acid hydrolysis of the oxime (III) followed by acetylation and chromatography gave the conjugated ketone (IV), m.p. 120—120·5°, λ_{max} (EtOH) 247 nm (ϵ 4300), ν_{max} (KBr) 1656 and 1620 cm^{-1}, in good yield, which was identical with a sample prepared from 3β-acetoxy-19-norcholest-5-ene.[3]



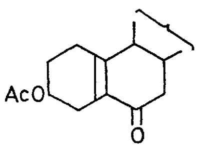
(I) a R=H
b R=NO



(II)



(III)



(IV)

The above results show that the migration of the NO group in the photolysis of (Ib) is accompanied by elimination of the angular hydroxymethyl group attached to the allylic position of the double bond.

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