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STEROIDS XXIX[1]. REACTIONS OF SOME STEROIDAL HYDROXYAZIDES. CONTRACTION OF RING B

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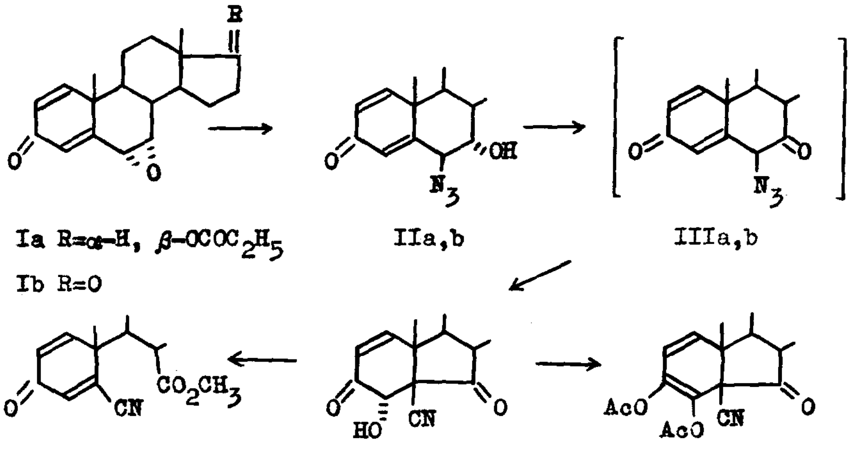
The epoxides Ia,b[2] were cleaved by hydrazoic acid[3] to yield 7α-hydroxy-6β-azido-1,4-diene-3-ketones IIa,b. Jones oxidation of the latter produced in moderate yield (up to 60%) the new compounds IVa,b to which the structure of B-nor-5-cyano-4α-hydroxy-1-ene-3,6-diones was ascribed on the basis of spectroanalytical and chemical evidence. IVa, uv (EtOH) 231 nm, ir (nujol) 3595, 2250, 1760, 1730, 1685 cm^{-1}, pmr (CDCl$_3$, δ) 6.84 (1H, d, J=10 Hz, H-1) 6.06 (1H, d, J=10 Hz, H-2), 4.41 (1H, s, H-4) ppm. The B-norketones IVa,b acetylated at rt gave the diacetates Va,b. Va, uv (EtOH) 260 nm, ir (nujol) 2240, 1780, 1760, 1725 cm^{-1}, pmr (CDCl$_3$, δ) 5.81 (2H, ABq, H-1 and H-2) ppm.



Ia R=α-H, β-OCOC$_2$H$_5$

Ib R=O

IIa,b

IIIa,b

VIa,b

IVa,b

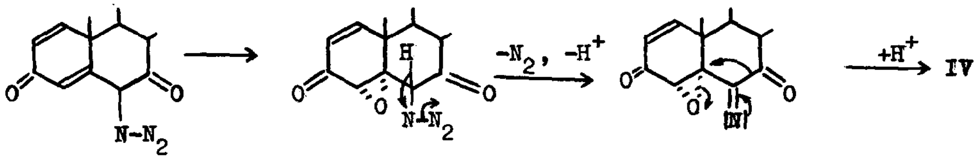
Va,b

Traces of alkali in methanol converted IVa or IVb resp. to the seco compounds VIa,b with a cross conjugated double bond system in A ring. VIa, uv (EtOH) 245 nm, ir (nujol) 2220, 1725, 1670 cm^{-1}, pmr (CDCl$_3$, δ) 6.84 (1H, d, J=10 Hz, H-1), 6.28 (1H, dd, J=10.5 Hz and 1.5 Hz, H-2), 6.76 (1H, d, J=1.5 Hz, H-4) ppm.

The low position4) of H-19 signal (1.45 for IVa) suggests that in this case the CN group must assume the β-orientation. The hydroxyl at C-4 accepts the α-configuration; this follows from the reaction mechanism as well as from the solvent shifts of pmr spectra5).

The formation of IVa,b formally resembles the rearrangement of some p-benzoquinone azides, reported by Moore6) and the fragmentation of some cyclic olefins with $C_6H_5J(OAc)_2$-$(CH_3)_3SiN_3$, recently described by Zbiral7). In these cases the azido group gave rise to the formation of a cyanide; however the reaction mechanism did not involve an oxidation. We postulate, that the first obvious step in Jones oxidation of our hydroxyazides is the oxidation of the secondary alcohol group at C-7. The ketoazides IIIa,b thus formed undergo most probably a second oxidation to an unstable epoxide, which can rearrange in different ways. One of them is presented below.

Further work is in progress and will be published with full analytical and spectral data.



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