

STEROIDS XVIII¹⁾. AN INTRAMOLECULAR MICHAEL REACTION OF
2 α -(2'-NITROETHYL)-17 α -METHYL-4-ANDROSTEN-17 β -OL-3-ONE

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In our earlier paper²⁾ we described the Michael reaction of nitromethane with 2-methylene-17 α -methyl-4-androsten-17 β -ol-3-one (I) leading to 2 α -(2'-nitroethyl)-17 α -methyl-4-androsten-17 β -ol-3-one (II).

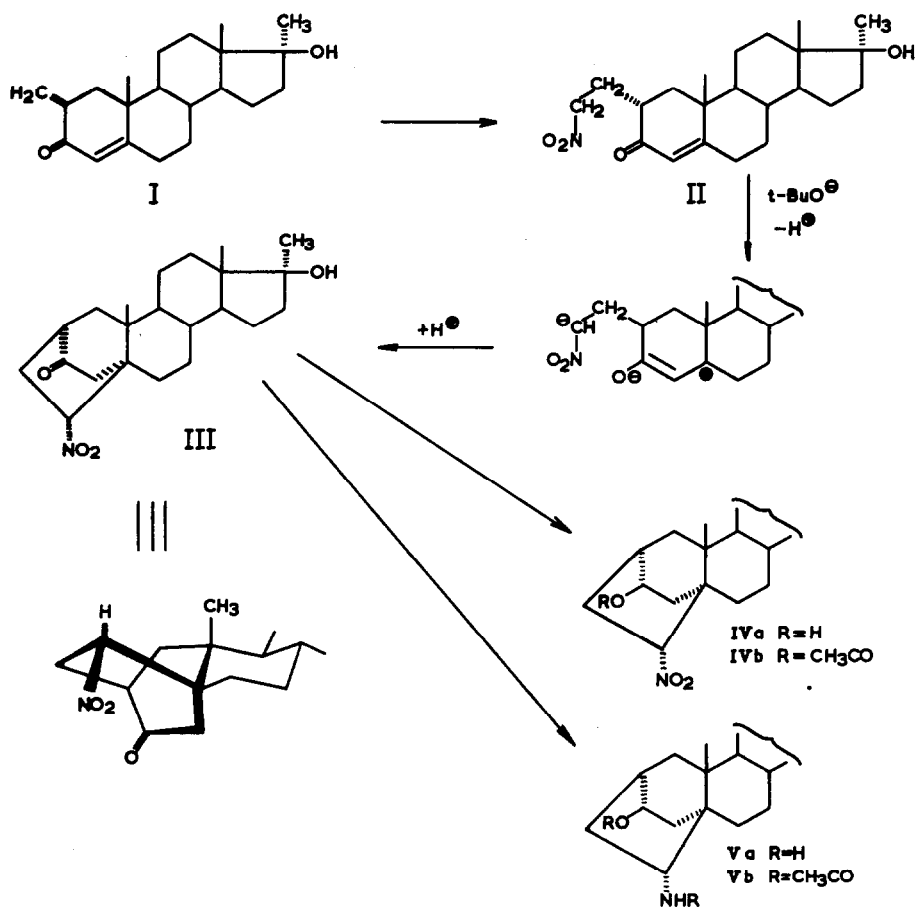
In the mother liquor of the latter compound and also on leaving it in an alkaline medium for several days we detected a new isomeric product (ca 9%), to which the structure III could be ascribed on the basis of its spectral properties. This new product does not absorb in UV, its IR contains only a sharp band at 1712 cm⁻¹ (sat. CO) and a band at 1548 cm⁻¹ (NO₂). The NMR shows one proton multiplet centered at δ 4.95 ppm assigned to the hydrogen atom bearing the NO₂-group, the usual signals of the methyl groups and no vinylic proton. The mass spectrum also confirms the proposed structure.

The formation of the new ring-A-bicyclic steroid could be explained as the epimerisation at carbon atom 2 leading to 2 β -(2'-nitroethyl)-substituent, giving rise to an internal Michael addition between the negative charged carbon atom 2' and the positive charge on carbon atom 5. The new compound exhibits a slightly positive Cotton effect (0.82 at 322 nm) which supports, on the basis of the octant rule, the proposed geometry i.e. the position of the new ring above the former ring A.

The bicyclic product III was reduced by NaBH₄ to the 3 β -alcohol IVa, monoacetylated to IVb. In the IR spectrum of the former a strong intramolecular hydrogen bonding between the hydroxylic proton and the nitro group was visible, thus supporting the geometry of the latter shown in the diagram.

The reduction of III with zinc dust - 50% acetic acid yielded an unstable amine Va, characterised as the N-acetyl- β acetate Vb.

All new compounds (III — Vb) gave satisfactory microanalyses and their spectral data were consistent with the proposed structures.



References :

- 1) Part XVII on Steroids : Bull. de l'Acad. Polon. des Sci. 1970 in press
- 2) M. Kocór and W. Kroszczyński, Bull. de l'Acad. Polon. des Sci., Ser. Sci. Chim. 17, 269 (1969).