Photorearrangement of 5α-Androst-1-en-3-one in Concentrated Acid Solution

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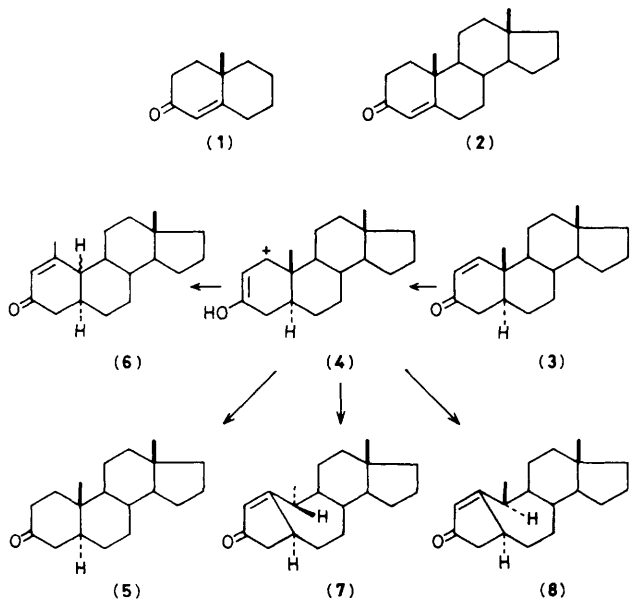
U.v. irradiation of the title compound in concentrated sulphuric acid gives mainly 5(10 → 1)*abeo* steroids.

While the irradiation of 10-methyloctalone (**1**) in concentrated sulphuric acid results in an interesting photoisomerization by the efficient rearrangement of the generated hydroxycation,[1] 4-androsten-3-one (**2**), under the same reaction conditions does not rearrange, being recovered unchanged.[2] We now report the irradiation of the isomeric enone, 5α-androst-1-en-3-



one [(3), λ_{max} (EtOH) 230 nm], which when dissolved in concentrated sulphuric acid forms a solution of the hydroxycation (4), absorbing at λ_{max} 270 nm.

Irradiation with a medium pressure Hg lamp of a concentrated sulphuric acid solution of (3), gave a mixture which was separated by SiO_2 chromatography and characterized.† Unreacted starting material (3) (19%);‡ a photoreduction product, 5α-androstan-3-one (5)[3] (18%), identical (mixed m.p., t.l.c., and i.r. and mass spectra) with an independent sample prepared by the Birch reduction of (2);[4] 1-methyl-19-nor-5α, 10ξ-androst-1-en-3-one (6) (5%), a compound which is also obtained, as the only reaction product, in the absence of light, being stable under the irradiation conditions; and finally, the two photoisomers 5(10 → 1)*abeo*-5α,10α- and 5(10 → 1)*abeo*-5α-androst-1-en-3-one, (7) and (8) (24% and 29%, respectively), were identified.

Compounds (7) and (8) are, to the best of our knowledge, the result of a new photochemical rearrangement in steroid chemistry, an interesting alternative to the photochemical behaviour of the same chromophore in neutral media, which is known to yield only dimerization products.[5]

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† All new compounds described provided the expected spectral data. The structures of the photoisomers (7) and (8) were further verified by *X*-ray analysis.

‡ Percentages based on g.l.c. analysis.