Some Observations of Oxygenation of C₂- or C₃-Oxo-5 α -steroids Possessing C₁₁-Oxo-group

Recently, Barton¹⁾ and Camerino²⁾ reported the oxygenation of various oxosteroids with oxygen in alkali medium, but the oxygenation of C₂- and C₃-oxosteroids possessing a C₁₁-oxo-group is not mentioned.

Here, the writers wish to compare the oxygenation of C₂- or C₃-oxo-5 α -steroids with the corresponding oxosteroids having a C₁₁-oxo-group, in order to examine whether or not the neighbouring effects of a C₁₁-oxo-group*¹ is shown on this oxidation reaction.

TABLE I.

Material	Oxidation Products			
	2,3-Dione	2-Hydroxy-1-en-3-one acetate	3-Hydroxy-3-en-2-one acetate	3,4-Dione
Cholestan-2-one	m.p. 163~167° (isolated as 2-hydroxycholest-1-en-3-one)	not isolate	m.p. 136.5~138° NMR : 3.86 τ (d)	
Cholestan-3-one	NMR : 3.65 τ (s)			
25D,5 α -Spirostan-2-one	NMR : 3.68 τ (s) 4.35 τ (d)	not isolate	m.p. : 237.5~240° NMR : 3.88 τ (d)	
25D,5 α -Spirostan-3-one	(as enols mixture)			
25D,5 α -Spirostan-2,11-dione	m.p. 233~237° UV : 270~271 m μ NMR : 3.25 τ (s)	m.p. 254~258° NMR : 2.88 τ (s)	m.p. 235~237° NMR : 3.89 τ (d)	m.p. 253~257° UV : 277~279 m μ NMR : 3.86 τ (s) ^{a)}
25D,5 α -Spirostan-3,11-dione	5.64 τ (d) (as enols mixture)			
17 β -Hydroxy-androstane-3,11-dione	m.p. : 170~173° UV : 270.5 m μ (ϵ 16,000) NMR : 3.20 τ (s)	m.p. : 202~203° ^{b)} UV : 236 m μ (ϵ 9,500) NMR : 2.83 τ (s)	m.p. : 225~228° ^{b)} UV : 238 m μ (ϵ 16,300) NMR : 3.87 τ (d)	m.p. : 187.5~192.5° UV : 277.5 m μ (ϵ 11,700~12,200) NMR : 3.84 τ (s)

a) The signal disappeared after D₂O was added.

b) Present values as diacetate.

As summarized in the accompanying table, C₂- or C₃-oxo-5 α -steroids were oxidized to the same C_{2,3}-dioxosteroid with oxygen. Both C₂- or C₃-oxosteroid having a 11-oxo group also gave the same 2,3,11-triketosteroid, but in the case of C_{3,11}-dioxo-steroid a small amount of 3,4,11-trioxosteroid*² was obtained. The latter was identified by the synthesis from 3,11-dioxo-5 β -steroid by the method reported by Camerino.²⁾ In view of the above facts, it is interesting to note that C₃-oxo-5 α -steroid is attacked at the position 2 by oxygen, but C_{3,11}-dioxo-5 α -steroid is attacked partially at C₄. It is probable that the distortion of A ring, due to the trigonal bond of the carbonyl group at C₁₁, somewhat changes the direction of enolisation in the case of C_{3,11}-dioxo-5 α -steroids.

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*¹ The neighbouring effects of C₁₁-substituents have been previously reported. For example, the addition reaction of 25D-5 β -spirost-2-ene with C₁₁-substituents was affected by the directing effects and gave an abnormal result. (K. Takeda, *et al.* : Steroids, 2, 27 (1963)).

*² The ratio of the formation of 2,3-dione and 3,4-dione is 9:1.

1) a) E. J. Bailey, J. Elks, D. H. R. Barton : Proc. Chem. Soc., 1960, 214. b) E. J. Bailey, D. H. R. Barton, J. Elks, J. F. Templeton : J. Chem. Soc., 1962, 1578.

2) B. Camerino, B. Patelli, R. Sciaky : Tetrahedron Letters, No. 16, 554 (1961).