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Some Observations of Oxygenation of C_2- or C_3-Oxo-5α-steroids Possessing C_{11}-Oxo-group

Recently, Barton[1] and Camerino[2] reported the oxygenation of various oxosteroids with oxygen in alkali medium, but the oxygenation of C_2- and C_3-oxosteroids possessing a C_{11}-oxo-group is not mentioned.

Here, the writers wish to compare the oxygenation of C_2- or C_3-oxo-5α-steroids with the corresponding oxosteroids having a C_{11}-oxo-group, in order to examine whether or not the neighbouring effects of a C_{11}-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 Cholestan-3-one	m.p. 163∼167° (isolated as 2-hydroxycholest-1-en-3-one) NMR : 3.65 τ (s)	not isolate	m.p. 136.5∼138° NMR : 3.86 τ (d)	
25D,5α-Spirostan-2-one 25D,5α-Spirostan-3-one	NMR : 3.68 τ (s) 4.35 τ (d) (as enols mixture)	not isolate	m.p. : 237.5∼240° NMR : 3.88 τ (d)	
25D,5α-Spirostan-2,11-dione 25D,5α-Spirostan-3,11-dione	m.p. 233∼237° UV : 270∼271 mμ NMR : 3.25 τ (s) 5.64 τ (d) (as enols mixture)	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 mμ NMR : 3.86 τ (s)[a]
17β-Hydroxy-androstane-3,11-dione	m.p. : 170∼173° UV : 270.5 mμ (ε 16,000) NMR : 3.20 τ (s)	m.p. : 202∼203°[b] UV : 236 mμ (ε 9,500) NMR : 2.83 τ (s)	m.p. : 225∼228°[b] UV : 238 mμ (ε 16,300) NMR : 3.87 τ (d)	m.p. : 187.5∼192.5° UV : 277.5 mμ (ε 11,700∼12,200) NMR : 3.84 τ (s)

a) The signal disappeared after D_2O was added.
b) Presont values as diacetate.

As summerized in the accompanying table, C_2- or C_3-oxo-5α-steroids were oxidized to the same $C_{2,3}$-dioxosteroid with oxygen. Both C_2- or C_3-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-5β-steroid by the method reported by Camerino.[2] In view of the above facts, it is interesting to note that C_3-oxo-5α-steroid is attacked at the position 2 by oxygen, but $C_{3,11}$-dioxo-5α-steroid is attacked partially at C_4. It is probable that the distortion of A ring, due to the trigonal bond of the carbonyl group at C_{11}, somewhat changes the direction of enolisation in the case of $C_{3,11}$-dioxo-5α-steroids.

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*[1] The neighbouring effects of C_{11}-substituents have been previously reported. For example, the addition reaction of 25D-5β-spirost-2-ene with C_{11}-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).