Configurational Effects in the Mass Spectra of Steroidal Polyketones

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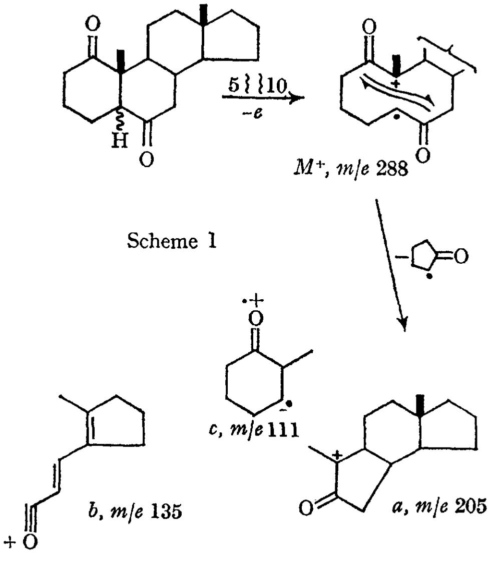
DURING microbiological studies of steroid transformations, the mass spectra of 1,6,17-trioxo- and 1,6-dioxo-5α- and -5β-androstanes were determined. The mass spectra of the thermodynamically more stable 5β-derivatives[3] showed very striking differences (Table) so much so that they were not initially recognized as 1,6-dioxo-steroids. The major ions from the 5α-compounds (Table), with the exception of the base peaks at *m/e* 219 and *m/e* 205 respectively, were a combination of the characteristic cleavages of 1-oxo- and 6-oxo-5α-androstane.[1,2] The base peaks were shown by high-resolution measurements to correspond to ions of composition $C_{14}H_{19}O_2$ and $C_{14}H_{21}O$ respectively, and intense metastable peaks at *m/e* 159·0 and 146·5 (calculated 158·5 and 146·0) indicated their formation from the molecular ions to be one-step processes. The fragmentation involved can be rationalised as shown in the reaction scheme. (The alternative loss of a fragment containing C-1, C-2, C-3, C-10, and C-19 was considered less likely since it requires cleavage of two bonds attached to C-10.)



Scheme 1

In the 5β-derivatives the base peak appears at *m/e* 111 (Table). High-resolution measurements showed this fragment to have the composition $C_7H_{11}O$ for all four compounds. Djerassi and his collaborators[1] suggest that in the case of 1-oxo-5α-androstane the ion (*c*) with *m/e* 111 (18% of base peak) results from homolysis of the C-9–C-10 bond followed by hydrogen radical transfer from C-8 to C-10 and homolysis of the C-5–C-6 bond. The greatly enhanced intensity of this peak in the mass spectra of the two 5β-androstanes can be explained by the easier fission of the C-9–C-10 bond resulting

TABLE

Major fragments in the mass spectra of some oxo-androstanes.

	M^+		$M-\dot{C}H_3$		$M-(\dot{C}H_3+CO)$		$M-C_4H_5O$[4]		*a*		*b*[5]		*c*	
	m/e	%	*m/e*	%	*m/e*	%	*m/e*	%	*m/e*	%	*m/e*	%	*m/e*	%
(I) 1,6,17-5α-	302	70	287	6	259	38	233	7	219	100	149	3	111	11
(II) 1,6-5α-	288	30	273	8	265	28	219	5	205	100	135	18	111	22
(III) 1,6,17-5β-	302	16	287	2	259	9	233	14	219	15	149	4	111	100
(IV) 1,6-5β-	288	22	273	5	265	8	219	23	205	21	135	11	111	100

in the relief of strain imposed on the 5β-compounds from interactions between the α-hydrogens of C-2, C-4, and C-9. Homolysis of the C-5–C-6 bond is facilitated in both series by the presence of the 6-oxo-function. Similar configurational effects have recently been reported for C-8, C-9, and C-10 epimeric testosterone derivatives.[6]

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[2] C. Djerassi, R. H. Shapiro, and M. Vandewalle, *J. Amer. Chem. Soc.*, 1965, **87**, 4892.

[3] J. E. Bridgeman, P. C. Cherry, W. R. T. Cottrell, Sir Ewart R. H. Jones, P. W. Le Quesne, and G. D. Meakins, *Chem. Comm.*, 1966, 561.

[4] Ref. 2, species (*R*).

[5] *cf.* Species (*S*) H. Budzikiewicz, C. Djerassi, and D. H. Williams, "Structure Elucidation of Natural Products by Mass Spectrometry, Vol. 2"; Holden-Day, San Francisco, 1964, p. 33.

[6] V. I. Zaretskii, N. S. Wulfson, and V. L. Sadovskaya, *Tetrahedron Letters*, 1966, 3879.