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Stereoselectivity in Reduction of Steroidal 7-Ketones*

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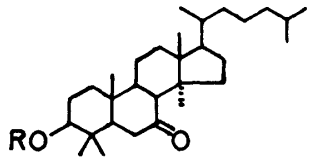
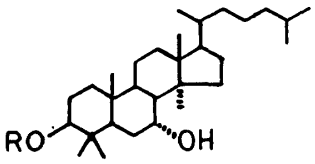
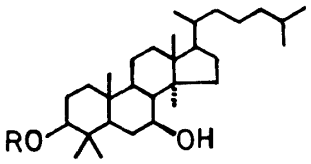
Several 7-ketones of lanostane, 4,4-dimethylcholestane and cholestane derivatives were subjected to catalytic hydrogenation on platinum, reduction with complex hydrides and reduction with sodium in *tert*-butanol, and the product ratios (7α-ol/7β-ol) were determined by gas chromatography or high-performance liquid chromatography. Catalytic hydrogenation of 3β-hydroxylanostan-7-one and 3β-hydroxy-4,4-dimethylcholestan-7-one yielded the 7β-alcohols as the major products, whereas their 3-acetates gave principally the 7α-alcohols. Reduction of various 7-ketones with sodium in *tert*-butanol gave mainly the 7β-equatorial alcohols, while the epimeric 7α-ols were the major products on reduction with lithium tri-*sec*-butylborohydride. The stereoselectivity of reduction with sodium borohydride and lithium aluminum hydride was highly dependent on the neighboring double bond and 4,4-dimethyl and/or 14α-methyl substituent(s).



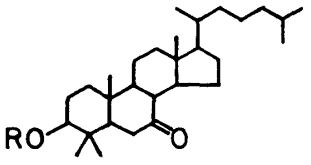
1a－c



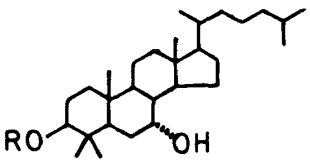
2a－c



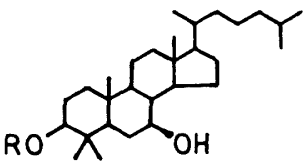
3a－c



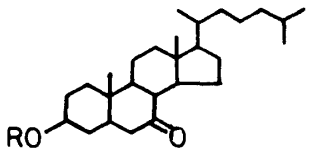
4a, b, d



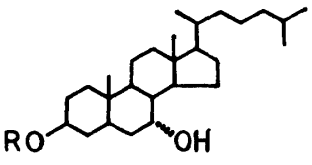
5a, b, d



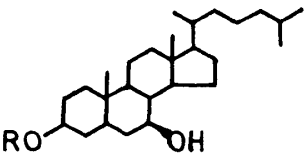
6a, b, d



7a, b, d



8a, b, d



9a, b, d

a: R=H **b**: R=Ac **c**: R=Ac, $\Delta^{8(9)}$ **d**: R=Ac, $\Delta^{5(6)}$

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Table I. Stereoselectivity in Reductions of Steroidal 7-Ketones

Substrate	Alcohols produced on reaction with				
	H_2/Pt 7α : 7β	Na/*tert*-BuOH 7α : 7β	$NaBH_4$ 7α : 7β	$LiAlH_4$ 7α : 7β	L-Selectride 7α : 7β
1 a	21 : 79	0 : 100	47 : 53	38 : 62	100 : 0
1 b	73 : 27	—	36 : 64	48 : 52	—
1 c	*a*)	—	62 : 38	71 : 29	*b*)
4 a	21 : 79	14 : 86	67 : 33	47 : 53	99 : 1
4 b	61 : 39	—	—	—	—
4 d	—	—	8 : 92	13 : 87	57 : 43
7 a	51 : 49	27 : 73	61 : 39	51 : 49	99 : 1
7 b	43 : 57	—	—	—	—
7 d	—	—	18 : 82	37 : 63	76 : 24

a) This reaction gave no 7-hydroxyl compound but yielded the $\Delta^{7,9(11)}$-diene and the $\Delta^{8(9)}$-olefin.
b) The starting ketone was recovered.