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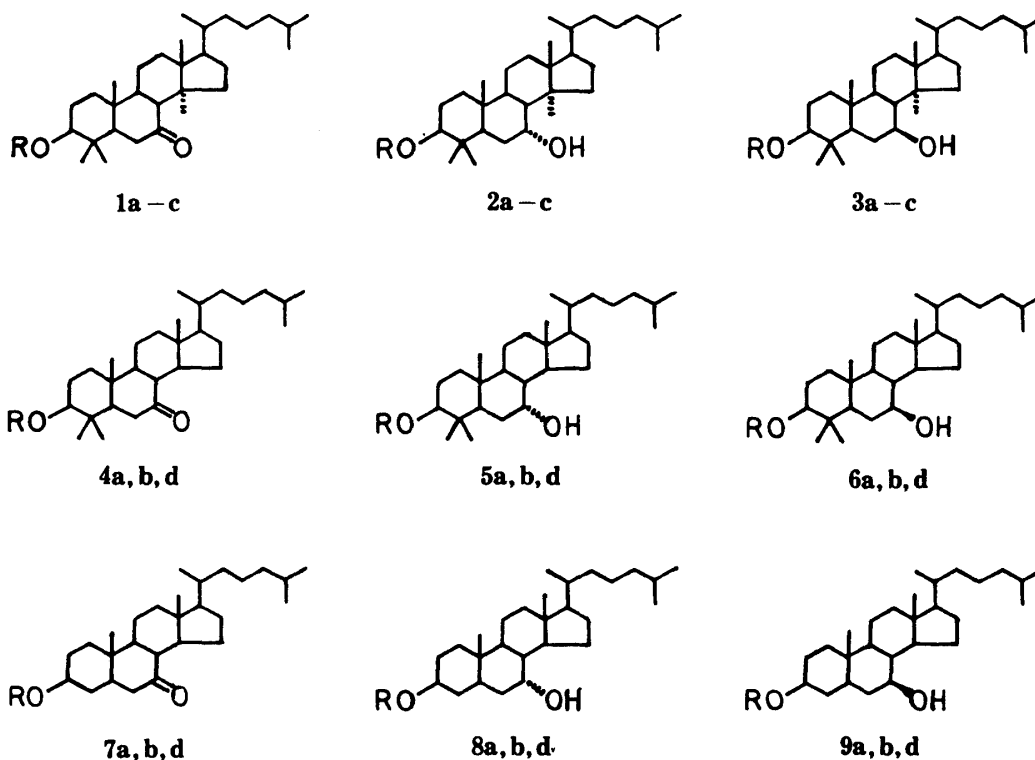
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Stereoselectivity in Reduction of Steroidal 7-Ketones*

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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).



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 7 α : 7 β	Na/ <i>tert</i> -BuOH 7 α : 7 β	NaBH ₄ 7 α : 7 β	LiAlH ₄ 7 α : 7 β	L-Selectride 7 α : 7 β
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.