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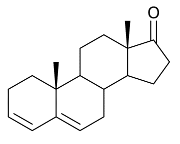
Regiospecificity of the Hydroboration of Some Steroidal *trans*-Dienes

Juliette A. Boynton, James R. Hanson* and Mansur D. Liman

School of Chemistry, Physics and Environmental Science, University of Sussex, Brighton, Sussex BN1 9QJ, UK

Hydroboration of 17β-hydroxy-3-methyleneandrost-4-ene gives 3β-hydroxymethyl-5α-androstan-4α,17β-diol whilst, contrary to previous reports, hydroboration of a steroidal 3,5-diene and a 4,6-diene affords not only the 4α,6α-diol but also the 3β,6β- and 4β,6α-diols from the 3,5-diene and the 4β,6α- and 4β,7β-diols from the 4,6-diene.



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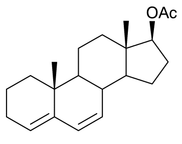

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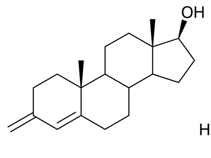

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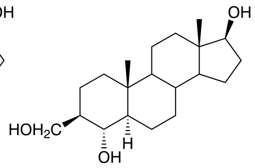

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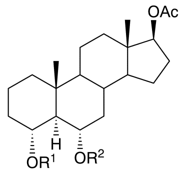
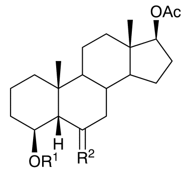
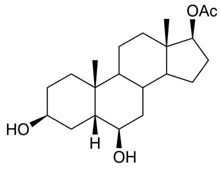


10 $R^1 = R^2 = Ac$
11 $R^1 = Ac; R^2 = H$
12 $R^1 = H; R^2 = Ac$
13 $R^1 = R^2 = H$



14 $R^1 = Ac; R^2 = \alpha\text{-OAc}, \beta\text{-H}$
15 $R^1 = Ac; R^2 = \alpha\text{-H}, \beta\text{-OH}$
16 $R^1 = H; R^2 = \alpha\text{-OH}, \beta\text{-H}$



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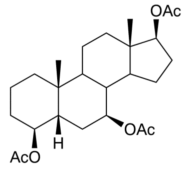

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The products of the hydroboration of cycloalkenes have been rationalized[2] in terms of the *cis*-addition of borane to the less hindered face of the alkene in an anti-Markownikoff manner. The hydroboration of buta-1,3-diene has been shown[4,5] to produce 1,3- and 1,4-butanediols in a 3:7 ratio. The directing influence of one alkene on the reactions of the other which led to the 1,3-diol, was offset by the introduction of alkyl substituents and 2,3-dimethyl-1,3-butadiene was converted almost exclusively to the 1,4-diol. The results were interpreted in terms of boracycle formation. However the hydroboration of both cholesta-3,5- and cholesta-4,6-diene have been reported[6] to give entirely a 1,3-diol, cholestan-4α,6α-diol.

The rigidity of the steroid ring systems permits an assessment of the different factors which contribute to the regio- and stereo-chemistry of the reaction which it is more difficult to make with the more flexible acyclic buta-1,3-diene. The results of hydroboration of androsta-3,5-dien-17-one (**5**), 17β-acetoxyandrosta-4,6-diene (**7**) and 17β-hydroxy-3-methyleneandrost-4-ene (**8**) are given in Table 1. The position and stereochemistry of the diols, some of which were separated as their acetates, were established from their ^{1}H NMR spectra.

Unlike the distribution of products from simple buta-1,3-dienes, the products from these hydroborations were mainly 1,3-diols rather than 1,4-diols. Molecular models suggest that some of the 1,3-diols may be formed *via* four-membered cyclocarboboranes.

Techniques used: ^{1}H NMR, IR, chromatography Refs: 11

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Table 1 Hydroboration of steroidal dienes

Substrate	Product	Yield (%)
17β-Hydroxy-3-methyleneandrost-4-ene (**8**)	4α,17β-dihydroxy-3β-hydroxymethyl-5α-androstane (**9**)	71
4α,17β-Androsta-3,5-dien-17-one (**5**)	Products after acetylation	
	4β,6α,17β-triacetoxy-5β-androstane (**14**)	11
	4α,6α,17β-triacetoxy-5α-androstane (**10**)	19
	4α,17β-diacetoxy-6α-hydroxy-5α-androstane (**11**)	6
	17β-acetoxy-4α,6α-dihydroxy-5α-androstane (**13**)	5
	17β-acetoxy-3β,6β-dihydroxy-5β-androstane (**17**)	11
17β-Acetoxyandrosta-4,6-diene (**7**)	Products after acetylation	
	4β,6α,17β-triacetoxy-5β-androstane (**14**)	11
	4α,6α,17β-triacetoxy-5α-androstane (**10**)	16
	4β,7β,17β-triacetoxy-5β-androstane (**18**)	6
	4β,17β-diacetoxy-6β-hydroxy-5β-androstane (**15**)	8
	17β-acetoxy-4β,6α-dihydroxy-5β-androstane (**16**)	8
	4α,17β-diacetoxy-6α-hydroxy-5α-androstane (**11**)	8
	6α,17β-diacetoxy-4α-hydroxy-5α-androstane (**12**)	

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*To receive any correspondence.