The Acid-catalysed Rearrangement of 3β,6β-Diacetoxy-9β-cholestan-5α-ol

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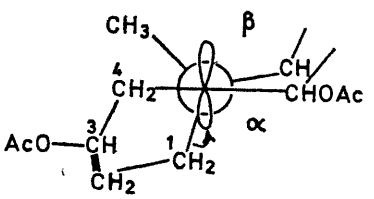
Summary Rearrangement of the 9β-cholestan-5α-ol(4) gives spirans (5) and (6) with retention of configuration at C-5.

RECENTLY it has been suggested[1] that, for the reaction of a 5α-hydroxy-steroid (1) with sulphuric acid in acetic anhydride–acetic acid to give[2] the 5β-alkyl-19-nor-Δ^9-compound (2), the increased rate of rearrangement (5·3 ×) for the 10β-ethyl-steroid (1a), relative to that for the 10β-methyl compound (Ib), pointed to participation by the angular alkyl group in the rate-determining heterolysis of the 5-acetyl sulphate (3).[3] Changes in inductive and minor steric effects on replacement of the 10β-methyl substituent by an ethyl group can, however, adequately account for this difference in rate without invoking anchimeric assistance by the alkyl group.

Reaction of the 9β-cholestan-5α-ol (4)[4] under the same conditions proceeded more rapidly (150×) than that for the 9α-compound (Ib) and gave the spirans (5; 70%) and (6; 17%). These products arise by the formation of a C-1–C-5 bond with *retention* of configuration at C-5 (Figure).



FIGURE

This marked increase in rate for the 9β-compound (4), in which neighbouring group participation is not possible, must be rationalised in terms of the relief of strain in the transition state for C-5–O bond heterolysis; in this transition state C-5 will be nearly planar and much of the strain of the original 5α,8β,9β,10β- system will be relieved.

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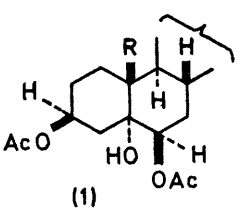
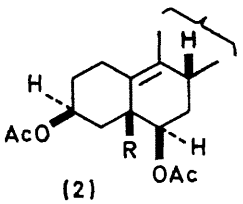
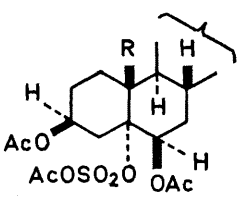


(1)

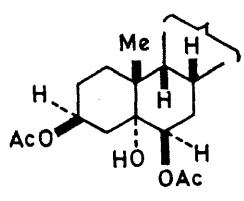
a; R = Et
b; R = Me



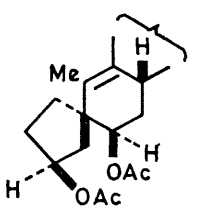
(2)



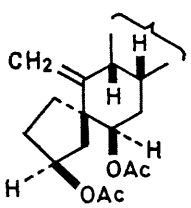
(3)



(4)



(5)



(6)

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[3] J. W. Blunt, A. Fischer, M. P. Hartshorn, F. W. Jones, D. N. Kirk, and S. W. Yoong, *Tetrahedron*, 1965, **21**, 1567.
[4] J. M. Coxon, M. P. Hartshorn, and C. N. Muir, to be published.