A Backbone Rearrangement in the 9β-Cholestane Series. Evidence for a Stepwise Mechanism

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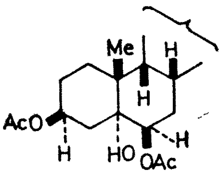
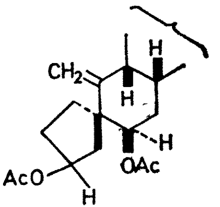
Summary The 5α-hydroxy-9β-cholestane compound (**1**) undergoes partial backbone rearrangement to the Δ^7-diacetate (**3a**) by a stepwise mechanism.

WHILE the backbone rearrangements of C-5 carbonium ions in the "normal" steroid series are considered to proceed by a stepwise mechanism involving a series of intermediate carbonium ions, evidence for this mechanism is limited. In support of the stepwise mechanism we now report a partial backbone rearrangement involving the *trans-syn-cis* system of the 5α-hydroxy-9β-cholestane derivative (**1**).

Reaction of 3β,6β-diacetoxy-9β-cholestan-5α-ol (**1**)[1] with thionyl chloride–pyridine at 20° gave, in addition to the known spiran (**2**) (70%),[2] a diacetate (23%) to which the rearranged Δ^7-structure (**3a**) was assigned on the following evidence. For the diol (**3b**), obtained from the diacetate (**3a**) by reaction with lithium aluminium hydride, the 6α-H signal was shown (double irradiation) to be coupled to the vinylic 7-H. Oxidation of the diol (**3b**) gave the diketone shown by its i.r. (ν_{max} 1727 and 1680 cm^{-1}) and u.v. spectra [λ_{max} (cyclohexane) 229·5 (ε 6070), 239 (6210), and 251 nm



(1)



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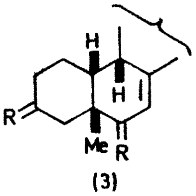

(3)

a; R = β-OAc, α-H
b; R = β-OH, α-H
c; R = O

TABLE

N.m.r. data[a] *for the rearranged* Δ^7*-olefins*

Compound	5β-Me	3α-H	6α-H	7-H	Others
(**3a**)	1·24	5·30	5·30	5·58(7 Hz)	2·01, 2·08 (OAc)
(**3b**)	1·18	4·33(13 Hz)	4·21(8 Hz)	5·79(7 Hz)	1·78(OH)
(**3c**)	1·47			6·48(1 Hz)	

[a] Determined at 60 MHz for $CDCl_3$ solutions containing $CHCl_3$ and tetramethylsilane as internal standards.

(6360)] to contain two six-membered ring carbonyl groups, one of which was conjugated. In the n.m.r. spectrum (see Table), the marked downfield shift (0·29 p.p.m.) of the 5β-methyl resonance on oxidation of diol (**3b**) is consistent[3] with its location adjacent to the C-6 oxygen function.

Full details of this and other related studies will be published later.

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[1] J. M. Coxon, M. P. Hartshorn, and C. N. Muir, to be published.

[2] J. M. Coxon, M. P. Hartshorn, and C. N. Muir, *Chem. Comm.*, 1970, 1591.

[3] J. W. Blunt, M. P. Hartshorn, and D. N. Kirk, *Tetrahedron*, 1966, 22, 3195.