

ACTIONS OF EPOXIDES - XXII* 4 α -HYDROXY COMPOUNDS FROM
4 β ,5-EPOXY-5 β -CHOLESTANE BY BF₃-CATALYSED REARRANGEMENT

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Brief (2 min.) reaction of 4 β ,5-epoxy-5 β -cholestane (1) with BF₃-etherate in benzene solution gave a crude product separable by chromatography. In addition to a mixture of cholesta-3,5-diene and cholesta-4,6-diene (total 8%), 5 α -cholestan-4-one (41%), and 5 α -fluorocholestan-4 β -ol (3%), three products were identified which had undergone skeletal rearrangement.

The 4 α -hydroxy- Δ^9 -compound (2; 11%), m.p. 82-83 $^\circ$, $[\alpha]_D + 43^\circ$, $n_{max} 3640$, 3600 cm.⁻¹, δ 0.80^{**} (C¹⁸H₃), 0.82 and 0.92 (side chain CH₂), 1.08 (5 β -CH₃), and 3.45 ppm ($W_{h/2}$ 6 cps; equatorial 4 β -H) was identified as follows. The location of the tetrasubstituted double bond ($\epsilon_{205\text{ nm}} 11,300$) was established by oxidation with CrO₃-pyridine¹ to give the known² β,γ -unsaturated ketone (3). The appearance of the C⁴H_{OH} proton in the NMR spectra of (2) and the epimeric 4 β -hydroxy-compound (4) reported earlier² provides additional support for the structural assignment.

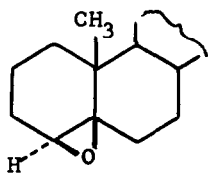
The remaining two compounds were assigned the 4 β -hydroxy- $\Delta^{13(17)}$ - (5; 23%), and 4 α -hydroxy- $\Delta^{13(17)}$ - (6; 3%) structures. The 4 β -hydroxy- $\Delta^{13(17)}$ - compound (5), identical with an authentic sample², and the epimeric alcohol (6) both gave the known 4-ketone (7) on oxidation.

The 4 β ,5 β -epoxide (1), m.p. 64-65 $^\circ$, $[\alpha]_D + 6^\circ$ (lit. values³: m.p. 60-62 $^\circ$, $[\alpha]_D + 3.5^\circ$), used in the rearrangement was prepared from 4 β ,5 α -diacetoxy-cholestane by reaction with KOH-ethanol³. Complete analysis (98%) of the products of BF₃-catalysed rearrangement of 4 α ,5-epoxy-5 α -cholestane revealed no trace of the 4 α -hydroxy- Δ^9 -compound (2). Compound (2) must therefore be regarded as a genuine product of BF₃-catalysed rearrangement of the 4 β ,5 β -epoxide (1).

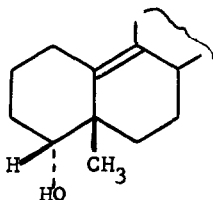
A full account of this and other related work will be published later.

References

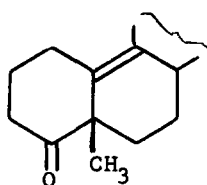
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 ** Determined at 60Mc for CDCl_3 solutions.
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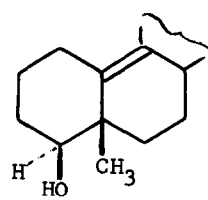
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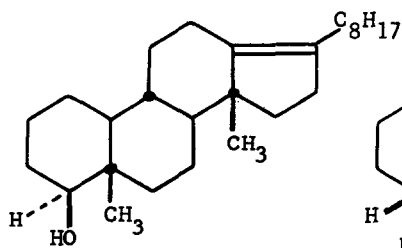
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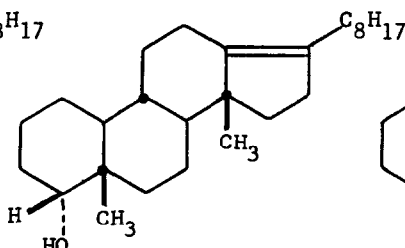
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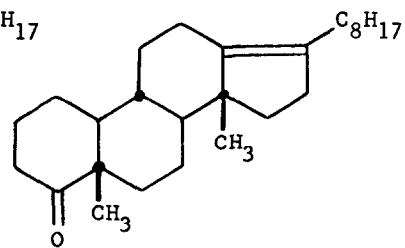
(4)



(5)



(6)



(7)