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REACTIONS OF 5α-HYDROXY STEROIDS PART VI[≠]
A BACK-BONE REARRANGEMENT OF
3β, 5α, 6β-TRIACETOXYCHOLESTANE

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Snatzke and Fehlhaber[1] reported the isolation, in yields up to 50%, of an unsaturated diacetate on treatment of the triacetate (I) with acetic anhydride in the presence of a variety of acidic catalysts at 80° or 140°. These authors tentatively assigned structure (II) to the diacetate but later commented (as a footnote) that the mass spectrum suggested an 18-nor-8β-methyl-$\Delta^{13(14)}$-partial structure.

This unsaturated diacetate is now shown to have structure (IIIa) in which the steroid skeleton has undergone a back-bone rearrangement. The assigned structure is supported by ultraviolet and N.M.R. spectra and conversion into a known compound. In particular, the ultraviolet spectrum (ε_{2050}, 11,200; ε_{2100}, 8,300; ε_{2150}, 5,300; ε_{2200}, 2,600) is consistent with a tetra-substituted double bond, exocyclic to at least one ring; the absence of vinylic protons is confirmed by the N.M.R. spectrum.

[≠] Part V: M.P. Hartshorn and D.N. Kirk, Tetrahedron, 1966, in press.

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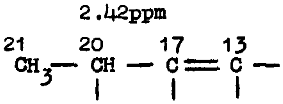
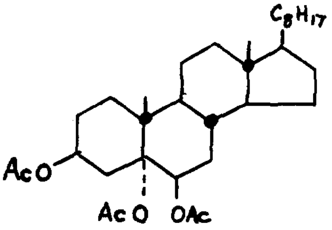
Hydrolysis of the diacetate (IIIa) gave a diol (IIIb) which on oxidation with 8N-chromic acid in acetone yielded the known[2] diketone (IIIc), the two samples being identical by infrared and N.M.R. spectra, and optical rotation.

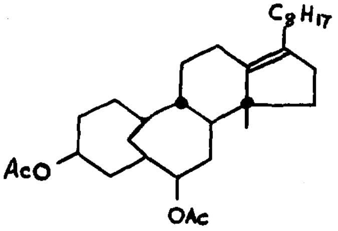
The N.M.R. spectra for the diacetate (IIIa), diketone (IIIc) and other related compounds reported earlier[2] support the assignment of a 13,17-olefin as opposed to a 13,14-olefin structure. For these compounds the 21-CH_3 group gives rise to a doublet, 1.00 and 0.90ppm, which on double irradiation with a frequency *ca*. - 88 cps is reduced to a singlet. This constitutes evidence for a partial structure.



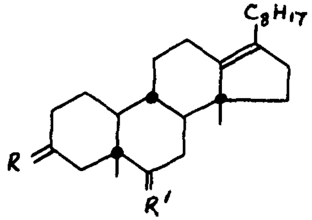
$$\overset{2.42\text{ppm}}{}\qquad \overset{21}{CH_3}-\overset{20}{\underset{|}{CH}}-\overset{17}{\underset{|}{C}}=\overset{13}{\underset{|}{C}}-$$



I



II



III

(a) R, R'; β OAc, H.
(b) R; βOAc, H : R'; αOAc, H.
(c) R, R'; β OH, H.
(d) R, βOH, H : R'; αOH, H.
(e) R, R'; O
(f) R; O : R'; βOH, H.

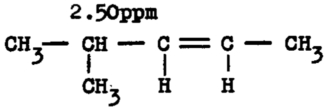
Table I N.M.R. Data (in ppm) for $\Delta^{13(17)}$- Derivatives[*]

	5β-Me	14β-Me	21-Me	26,27-Me	3-H	6-H
IIIa	1.02	0.90	1.00, 0.90	0.89, 0.79	4.97(6)[≠]	4.47(12)
IIId	1.08	0.90	1.02, 0.92	0.89, 0.80	5.05(7)	4.57 (5)
IIIb	1.08	0.91	1.00, 0.90	0.89, 0.79	4.17(6)	3.25(12)
IIIe	1.15	0.90	1.00, 0.90	0.90, 0.80	4.20(7)	3.40 (8)
IIIc	1.05	0.98	1.00, 0.90	0.90, 0.80	-	-
IIIf	0.78	0.90	1.02, 0.92	0.90, 0.80	-	3.33(14)

[*] For CCl_4 solutions at 60Mc with $CHCl_3$ and $(CH_3)_4Si$ as internal standards.

[≠] Width at half-height (cps).

For an analogous structure



$$\mathrm{CH_3{-}\overset{2.50ppm}{\underset{CH_3}{CH}}{-}\underset{H}{C}{=}\underset{H}{C}{-}CH_3}$$

the gem-dimethyl protons give rise to a six-proton doublet at 1.00 and 0.90ppm, the doublet arising from the interaction of the methyl protons with the adjacent methine proton (2.50ppm).

Finally, the methyl proton region of the N.M.R. spectra of the above related compounds (IIIc), (IIIa) etc. may be analysed as shown in Table I. These data provide clear evidence for a 5β-methyl-structure and militate against the 5,10-bridge structure (II) proposed[1] originally by Snatzke and Fehlhaber. Furthermore an additional compound, the 3-keto-6β-alcohol (IIIf), which also gives rise to the diketone (IIIc) on oxidation, gave a Cotton curve (*a* - 66) consistent with the 5β-methyl-10α-H-structure here proposed.

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2. J.W. Blunt, M.P. Hartshorn and D.N. Kirk, Chem. Comm., 1966, in press.
3. J.W. Blunt, M.P. Hartshorn and D.N. Kirk, forthcoming paper.