A Convenient Preparation of 5α-Androstan-16-one

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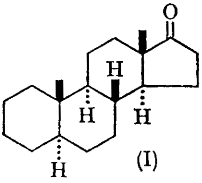
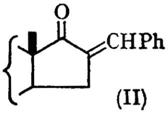
IN continuing studies with oxo-steroids, we required a substantial amount of 5α-androstan-16-one (IV). The best previous route[1] from the readily available 17-ketone (I) involves reduction of its 16-hydroximino-derivative to the 17β-hydroxy-16-ketone: removal of the 17-hydroxy-group required three more operations, and although each stage of this sequence is efficient (overall yield 52%), the process is somewhat lengthy.

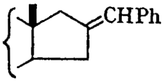
Of the methods we investigated, the most convenient involves only three steps. Condensation of the 17-ketone with benzaldehyde gave the conjugated ketone (II; 96%), which was reduced with lithium aluminium hydride and aluminium chloride to the 16-benzylidene derivative (III; 90%). Ozonolysis (95% yield) of the latter produced the 16-ketone (IV) in 82% overall yield. In developing this route, various products were obtained by reducing the conjugated ketone (II) in different ways. For example, hydrides alone simply afforded the 16-benzylidene-17β-alcohol, while treatment with excess of zinc and acetic acid at 20° gave equal amounts of this alcohol and the 16β-benzyl-17-ketone.



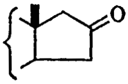
(I)



(II)



(III)



(IV)

The structures of the new compounds were supported by spectroscopic examination, the configurations at the 16- and 17-positions following from the n.m.r. and o.r.d. measurements.

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[1] D. Varech and J. Jacques, *Bull. Soc. chim. France*, 1965, 67.