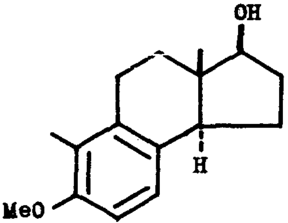
Tetrahedron Letters No.20, pp. 1879-1881, 1967. Pergamon Press Ltd. Printed in Great Britain.

THE TOTAL SYNTHESES OF 17β-HYDROXY-DES-A-ANDROST-9-ENE-5-ONE AND 17β-HYDROXY-10α-DES-A-ANDROSTAN-5-ONE*

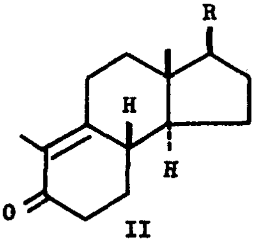
D. K. Banerjee, P. S. N. Murthy and V. Paul
Department of Organic Chemistry, Indian Institute of Science,
Bangalore, India

(Received 6 March 1967)

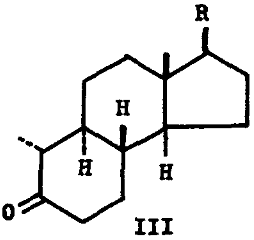
SYNTHESES of 8-isotestosterone and the corresponding anthracene analogue using <u>trans</u>-1β-hydroxy-8-methyl-4,5-(3'-methyl-4'-methoxybenzo)-hydrindane (I) were earlier reported[1]. The present communication describes the preparation of 17β-hydroxy-des-A-androst-9-ene-5-one (IIR=OH) and 17β-hydroxy-10α-des-A-androstan-5-one (IIIR=OH) and their benzoates, as possible intermediates for the synthesis of other steroids, from I. Optical antipodes of these compounds were previously obtained by Hartshorn and Jones[2] by the degradation of testosterone acetate.



I



II



III

R=OH, OBz

Lithium-liquid ammonia-ethanol reduction of I under specific conditions gave the unsaturated keto-alcohol (IIR=OH) as its 2,4-DNP, m.p. 205°; UV λ_{max}^{EtOH} 226 mμ ε 12,280, 259 mμ ε 13,860 and 387 mμ ε 23,920, in 24% yield. Pure IIR=OH,

---

* Steroid nomenclature. Melting points are uncorrected.

m.p. 131-133°; UV λ_{max}^{EtOH} 249 mμ ε 15,660; IR ν_{max}^{Nujol} 3650 cm^{-1}, 1654 cm^{-1}, 1610 cm^{-1} and 1064 cm^{-1}, could be obtained by regeneration[3] from its derivative. IR spectrum ($CHCl_3$) of the benzoate (IIR=OBz), m.p. 134-135°; UV λ_{max}^{EtOH} 237.5 mμ ε 22,500; IR $\nu_{max}^{CHCl_3}$ 1721 cm^{-1}, 1667 cm^{-1} and 1266 cm^{-1}, was identical with that of an authentic optically active sample.

Hydrogenation of IIR=OH and OBz over 2% Pd-$SrCO_3$ in ethanol in presence of 25% KOHaq gave IIIR=OH and OBz, m.p. 116.5-118° and 128.5-129.5°; IR ν_{max}^{Nujol} 3584 cm^{-1}, 1712 cm^{-1} and 1058 cm^{-1} and $\nu_{max}^{CS_2}$ 1724 cm^{-1} and 1275 cm^{-1} respectively. IR spectrum of IIIR=OBz was superimposable with that of an authentic optically active sample. This showed that the axial C-10 methyl group, resulting from the addition of hydrogen to II from the α-face of the molecule, had epimerized to the more stable equatorial conformation in presence of alkali.

Recently synthesis of an optical antipode of IIR=OH by an entirely different route has been reported[4].

Elemental analyses of the reported compounds agreed with their assigned structures.

Our sincere thanks are due to Professor E. R. H. Jones for the supply of authentic samples of IIR=OBz and IIIR=OH and OBz and for comparing the IR spectrum of IIIR=OBz with that of their material. We are grateful to the Council of Scientific and Industrial Research (India) for supporting the work with the award of a Research grant and Research Assistantship to one of us (P. S. N. M.).

REFERENCES

1. D. K. Banerjee, V. Paul and S. K. Balasubramanian, *Tetrahedron Letters*, 23 (1960); D. K. Banerjee, V. Paul, S. K. Balasubramanian and P. S. Murthy, *Tetrahedron*, **20**, 2487 (1964).
2. M. P. Hartshorn and E. R. H. Jones, *J. Chem. Soc.*, 1312 (1962).
3. J. Demaecker and R. H. Martin, *Nature*, **173**, 266 (1954).
4. Zoltan G. Hajos, David R. Parrish and Eugene P. Olivete, *Tetrahedron Letters*, 6495 (1966).