

Some Steroidal 22-Enes: the Synthesis of (a) Steroidal 22,24(28)-Dienes and (b) Ergosta-5,7,22,24(28)-tetraen-3 β -ol

By A. B. GARRY, J. M. MIDGLEY, W. B. WHALLEY,* and B. J. WILKINS

(The School of Pharmacy, The University, London, W.C.1)

Summary Dehydrobromination of 22,23-dibromo-5 β -ergostane yields the 22,24(28)-diene; application of this observation furnishes a novel, short route to ergosta-5,7,22,24(28)-tetraen-3 β -ol.

As part of an investigation into the synthesis of unsaturated steroids of potential biosynthetic significance we dehydro-

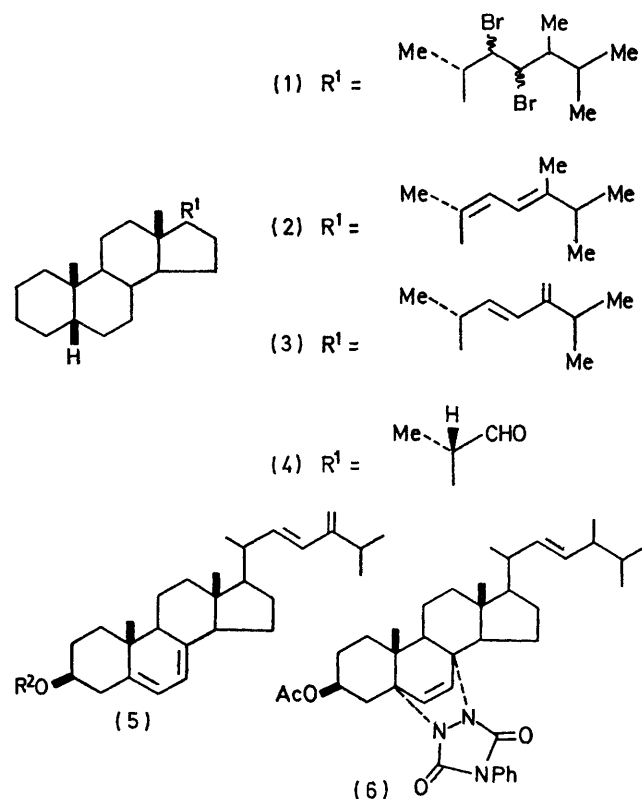
brominated 22,23-dibromo-5 β -ergostane (1) with 1,5-diazabicyclo[4,3,0]non-5-ene. Instead of the expected 20(22),23-diene (2) the isomeric 5 β -ergosta-22,24(28)-diene (3) was formed (80% yield). The structure of (3) was in accord *inter alia* with the n.m.r., u.v., and i.r. spectra and the formation of the aldehyde (4), and formaldehyde, upon ozonolysis. The constitution of the diene (3) has been confirmed by synthesis. Thus, ozonolysis of 5 β -ergosta-22-ene in 1% pyridine-methylene chloride at -70° gave the aldehyde (4), which failed to crystallise but furnished a crystalline 2,4-dinitrophenylhydrazone. Since the n.m.r. spectrum of (4) showed only one pair of doublets at τ 0.46 it was assigned the 20S-configuration (*cf.* ref. 1). Condensation of the aldehyde (4) in boiling ether-tetrahydrofuran with the ylid generated *in situ* from methyl-lithium and (3-methyl-2-methylenebutyl)triphenylphosphonium bromide¹ gave 5 β -ergosta-22,24(28)-diene (3), identical on the basis of $[\alpha]_D$, m.p., mixed m.p., n.m.r., i.r., u.v., and mass spectrum with that obtained from (1), which regenerated 5 β -ergost-22-ene quantitatively with zinc dust.

Application of this observation provides a short route from ergosterol, to the biosynthetically important¹ ergosta-5,7,22,24(28)-tetraen-3 β -ol (5; $R^2 = H$). Thus bromination of the adduct¹ (6) between ergosteryl acetate and 4-phenyl-1,2,4-triazoline-3,5-dione gave the 22,23-dibromo-adduct (80%). When this was heated under reflux in toluene containing 1,5-diazabicyclo[4,3,0]non-5-ene, in nitrogen during 18 h, elimination of hydrogen bromide and of the triazoline residue proceeded concomitantly to yield 3 β -acetoxyergosta-5,7,22,24(28)-tetraene (5; $R^2 = Ac$) having the requisite physical properties (65% yield).

Ergosteryl acetate was similarly regenerated in 73% yield from its adduct with 4-phenyl-1,2,4-triazoline-3,5-dione.

All new compounds exhibited the correct analytical and spectral characteristics.

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¹ D. H. R. Barton, T. Shioiri, and D. A. Widdowson, *J. Chem. Soc. (C)*, 1971, 1968: We thank Professor D. H. R. Barton, F.R.S., for supplying experimental details before publication.