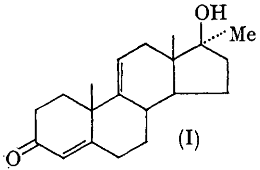
Steroidal Phenanthrenes

By W. BROWN and A. B. TURNER*

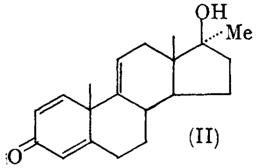
(*Department of Chemistry, The University, Aberdeen,* AB9 2UE)

IN developing new routes to ring A/B aromatic steroids, we have studied the reaction of 17α-methyl-$\Delta^{9(11)}$-testosterone (I; $[\alpha]_D = +56°$) with 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ). Initial dehydrogenation, using one equivalent of the quinone, followed the normal course[1] in refluxing dioxan to give the 1,2-dehydro-derivative (II; $[\alpha]_D = -97°$) in 84% yield. This material was probably contaminated with a small amount of the tetraene (III), which could not be removed. Further dehydrogenation of the trienone (II) took place readily with the aid of acid catalysts.[2] In the presence of toluene-*p*-sulphonic acid, the trienone (II) reacted with two equivalents of DDQ in refluxing dioxan. After 3 days, the only steroidal product was the optically inactive phenanthrene (V) resulting from migration of both angular methyl groups. The n.m.r. spectrum of this rearranged product, which was isolated in 48% yield, showed the presence of an aromatic methyl group (τ 6·98) and a *gem*-dimethyl group (τ 8·65). The aliphatic protons in ring D appeared as multiplets centred at τ 6·72 and 7·93.[3] Acetylation of the phenol (V) gave the monoacetate (VI). When the reaction was interrupted after 24 hr., the pentaene (IV) was obtained in 58% yield after chromatography on silica gel. The structure of the intermediate (IV) was clear from its spectral data. In particular, its n.m.r. spectrum exhibited a multiplet attributable to the C-16 olefinic proton at τ 4·65, coupled with the C-17 methyl group (multiplet at τ 8·34). The pentaene (IV) could not be crystallised, and was readily transformed into the crystalline phenol (V) during purification procedures. An aerial oxidation is probably involved here, although neither in this nor in the previous rearrangement is the precise sequence of oxidation and methyl migration steps yet established. The freshly chromatographed pentaene (IV) undergoes a similar double methyl migration, leading to the phenanthrene (VI), in refluxing acetic anhydride containing toluene-*p*-sulphonic acid.

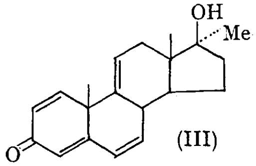
A number of rearrangements involving migration of the angular C-18 methyl group to C-17, with concomitant formation of a 13,14-double bond, have been reported recently.[4] Some, and conceivably all, of these involve a $\Delta^{17(20)}$-intermediate. The demonstration that the Δ^{16}-derivative (IV) is an intermediate in the aromatizations reported here suggests that an analogous mechanism, proceeding *via* a Δ^{16}-compound, could also operate in related rearrangements such as that used in the original proof of the structure of oestrone.[5] It is of interest, in this connection, that the tetraene (III), which has been prepared from the ketone (I) *via* its 6-dehydro-derivative, is quite stable—in contrast to its dehydration product (IV). Other factors, however, may contribute to the instability of the latter compound, and further work to determine these is in progress.



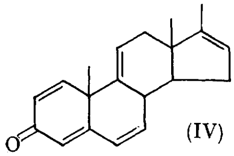
(I)



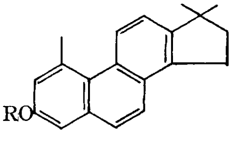
(II)



(III)



(IV)



(V) R=H
(VI) R=Ac

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[1] D. Burn, D. N. Kirk, and V. Petrow, *Proc. Chem. Soc.*, **1960**, 14.
[2] A. B. Turner and H. J. Ringold, *J. Chem. Soc.* (*C*), **1967**, 1720.
[3] M. S. Bharuca, E. Weiss, and T. Reichstein, *Helv. Chim. Acta*, **1962**, **45**, 103.
[4] F. Kohen, R. A. Mallory, and I. Scheer, *Chem. Comm.*, **1967**, 1019 and refs. therein; H. L. Herzog, O. Gnoj, L. Mandell, G. G. Nathansohn, and A. Vigevani, *J. Org. Chem.*, **1967**, **32**, 2906; E. A. Brown, *J. Medicinal Chem.*, **1967**, **10**, 546.
[5] A. Cohen, J. W. Cook, and C. L. Hewett, *J. Chem. Soc.*, **1935**, 445.