# Methyl Migration by Epoxide Cleavage. The Effect of Carbonium Ion Stabilisation by a Neighbouring Double Bond on the Direction of Migration on Cleavage of 9β,11β-Epoxy-4,4-dimethylandrost-5-ene-3,17-dione

By J. W. APSIMON* and J. M. ROSENFELD

(*Department of Chemistry, Carleton University, Ottawa, Canada*)

*Summary* The stabilisation of a developing cationic centre by an adjacent double bond has been found to direct the migration of the 10-methyl group to C-9 on cleavage of 9β,11β-epoxy-4,4-dimethylandrost-5-ene-3,17-dione.

As a part of our interest in the synthesis of cucurbitacins, *e.g.*, (**1**) we have studied the epoxide-cleavage-initiated migration of methyl groups[1] as a logical route to such systems, *e.g.*, (**2**) (arrows). We have attempted this transformation, unsuccessfully, in several lanostane derivatives.[2]

In our earlier steroidal examples[1] more than one migration pathway was followed; thus, we decided to incorporate a further controlling feature in the migration route. Reasoning that a developing allylic tertiary cation would be a favoured pathway[3] we cleaved epoxide (**3**) with $BF_3$ in benzene and obtained the dienedione (**4**) (m.p. 198—199°, $\nu_{max}$ 3480, 1735, and 1711 cm$^{-1}$, $\lambda_{max}$ 235 nm, $\epsilon$ 6150)† as the only product (t.l.c., >80% isolated yield).

The structure of (**4**) follows, besides spectral data, from its rearrangement in base to dieneone (**5**) (partial structure) ($\lambda_{max}$ 300 nm, $\epsilon$ 6150), and under milder basic conditions to the Michael addition product (**6**) (no strong u.v. absorption above 210 nm; no OH by i.r. and n.m.r.; $M^+$ 328, base peak of *m/e* 286, $M - CH_2 = C = O$: reverse Diels-Alder). This process can best occur with a *cis*-BC ring junction.[4]

Epoxide (**3**) was synthesised in an unexceptional manner from androst-4-ene-3,11,17-trione. An interesting facet of this synthesis is the stability of epoxide (**7**) to the basic conditions (KOBu$^t$, Bu$^t$OH) used for 4,4-dimethylation.[5]

This highly efficient and controlled methyl migration procedure shows promise for the synthesis of a variety of terpenoids besides the cucurbitacins.

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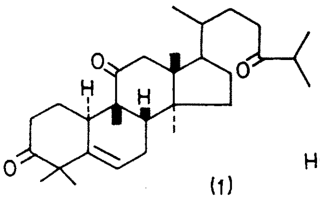

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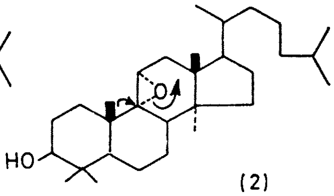

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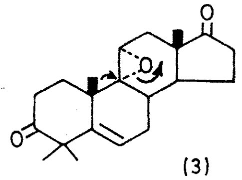

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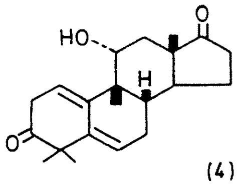

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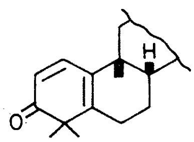

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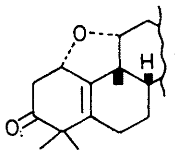

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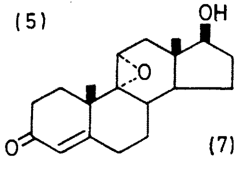

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† Satisfactory analyses, and n.m.r. and mass-spectral data, were obtained for the new compounds reported.

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[4] O. E. Edwards and T. Sano, *Canad. J. Chem.*, 1969, **47**, 3489.

[5] *Cf.*, B. Rickborn and R. P. Thummel, *J. Org. Chem.*, 1969, **34**, 3583; R. P. Thummel and B. Rickborn, *J. Amer. Chem. Soc.*, 1970, **92**, 2064, and references therein.