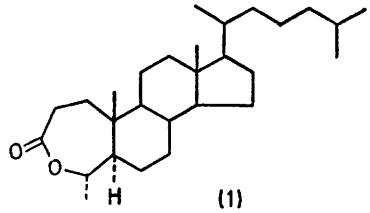
Exhaustive Baeyer–Villiger Oxidation of the *allo*-Betulone Triterpenoid

By TAPIO HASE

(Department of Chemistry, Helsinki University of Technology, Otaniemi, Finland)

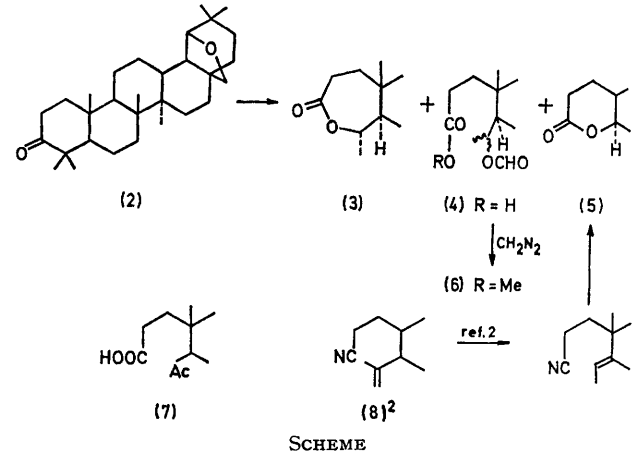
Summary Acid-catalysed peracetic acid oxidation of *allo*-betulone (2) gives the lactones (3) and (5) together with an acid (4).

4,4-DIMETHYLCHOLESTAN-3-ONE has been reported[1] to undergo acid-catalysed Baeyer–Villiger oxidation giving compound (1) (*i.e.*, the expected lactone minus the 4β-



(1)

methyl group), probably *via* an 8-stage mechanism. *m*-Chloroperbenzoic or perbenzoic acid and a mineral acid catalyst were used in that reaction; in an analogous reaction with compound (2) these reagents gave the lactone (3).† However, when commercial 40% peracetic acid together with 10% sulphuric acid in acetic acid–methylene chloride was used, two other major products, in addition to



SCHEME

† Stereochemistry at C-4a is based on analogy.[1] This lactone with unknown configuration at C-4 but with very similar physical data has been reported.[2]

(3), resulted. The more polar of these products was assigned structure (4) {methyl ester (6), m.p. 223—224° $[\alpha]_D$ +48·1°} and the less polar was assigned structure (5) {m.p. 249–250°, $[\alpha]_D$ + 127·5°}, on the basis of analytical and spectral data, chemical properties, and an alternative synthesis (Scheme).

Compound (4) is presumably formed by oxidation of the corresponding aldehyde, the related aldehyde being an established intermediate in the original cholestanone reaction.[1] Although (1) could have been formed in that reaction from an intermediate similar to (4) instead of from the aldehyde, the presence of such an intermediate was in fact shown to be unlikely.[1] However, acid treatment of (4) slowly gives (3). Various paths may be suggested for the formation of (5). The aceto-acid (7) may well be an intermediate, *cf.* the performic acid oxidation of the closely related nitrile (8)[2] which gave, among other products, a formate-nitrile and an acetyl-nitrile corresponding to (4) and (7), respectively.

Work is now in progress to establish the actual mechanism of formation of (5). The reaction may also lead to the development of an efficient new route for 4,4-demethylation at the terpenoid ring A, as a BF_3-catalysed reaction gives (5) in above 50% yield from (2). Several routes from (5) to the corresponding 4-en-3-one are being studied.

(*Received, 24th April* 1972; *Com.* 787.)

[1] J. S. E. Holker, W. R. Jones, and P. J. Ramm, *J. Chem. Soc.* (*C*), 1969, 357.
[2] J. Klinot, N. Hovorková, and A. Vystrčil, *Coll. Czech. Chem. Comm.*, 1970, **35**, 1105.

Printed by W Heffer & Sons Ltd Cambridge England