A Fragmentation Reaction leading to Aromatisation

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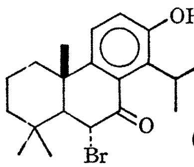
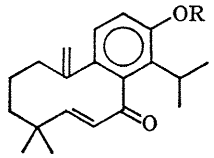
Summary On treatment with sulphuric acid in acetone, the mono-epoxide derivative (III) of the seco-diterpenoid (II) undergoes a novel aromatisation to a naphthalenic aldehyde (V) by successive transannular cyclisation and heterolytic fragmentation reactions.

WE have recently shown[1] that 6α-bromo-13-hydroxytotara-8,11,13-trien-7-one (I) undergoes a heterolytic fragmentation to the seco-diterpenoid (II, R = H) when treated with sodium hydrogen carbonate in dimethyl sulphoxide. In an attempt to effect a transannular cyclisation of the ten-membered ring of the methyl ether of the seco-diterpenoid (II; R = Me), its mono-epoxide derivative (III) was heated under reflux with sulphuric acid in acetone.[2] A single crystalline product, $C_{21}H_{28}O_3$, m.p. 109—111°, was obtained which was shown to be the naphthalenic aldehyde (V) from its n.m.r. and i.r. spectroscopic and chemical properties. The compound gave positive ferric chloride, Brady s, Fehling's, and silver-mirror tests.

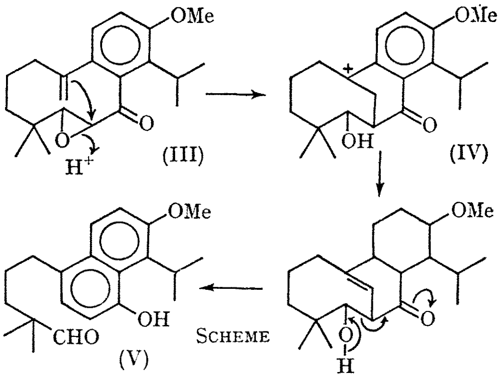


(I)



(II)

While aromatisation resulting from the action of an acid on an epoxy-ketone is known,[3] the formation of an aldehyde by a cyclisation–ring-opening reaction has not hitherto been observed. Its formation can be rationalised, however, according to the following scheme. Transannular attack by the π-electrons of the exocyclic double bond at C-6 with simultaneous opening of the protonated epoxide ring would give the tertiary carbonium ion (IV). Elimination with simultaneous or successive (as depicted) heterolytic fragmentation would then afford the naphthalenic aldehyde (V). The transannular cyclisation finds analogy in the recently reported cyclisation of a cumarinyl epoxide derivative[4] while fragmentation involving the system HO·C·C·C : O is well recognised.[5]



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