Reaction of Epoxides: a Novel Base-catalysed Rearrangement of Hydroxy-epoxides

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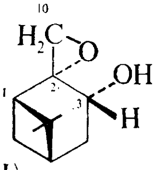
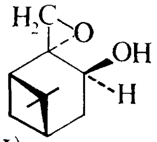
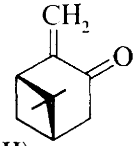
EPOXIDES of allylic alcohols may normally be derived from the corresponding acyloxy-epoxides by simple ester hydrolysis with mild aqueous alkali. We report the rearrangement of the 2,10-epoxy-10β-pinan-3-ols,[1] (I) and (II), on treatment with 0·125M-sodium hydroxide in aqueous methanol at 60°, to give essentially quantitative yields of pinocarvone (III). Both reactions are kinetically approximately first-order in epoxide and hydroxide ion, the rate of reaction of the 3β-hydroxy-epoxide (II) being greater (*ca.* 10 ×) than for the 3α-hydroxy-epoxide (I).



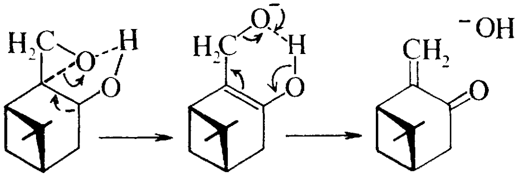
(I)



(II)



(III)



(IV)

We consider that the relative rates of reaction reflect the accessibility to hydroxide-ion approach of the proton at C-3. It seems probable that the abnormal ease of rearrangement of hydroxy-epoxides (I) and (II) with alkali is due to the participation of the suitably orientated 3-hydroxy-groups in the subsequent epoxide-ring opening (IV). The results from preliminary kinetic studies with appropriately deuteriated substrates are in accord with the mechanism proposed.

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[1] J. M. Coxon, E. Dansted, M. P. Hartshorn, and K. E. Richards, *Tetrahedron*, 1968, **24**, 1193.