The Base-catalysed Aromatisation of Dihydronaphthalenes

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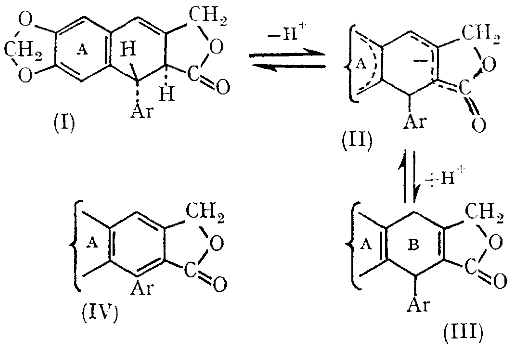
IT has been shown[1] that α-apopicropodophyllin (I) is converted by bases into the β-isomer (III), in which the B-ring has a less-strained boat-like conformation. The isolation[1] of only the α-apo-acid on alkaline hydrolysis of (III) must result from formation of (I) by the retro-reaction and the more rapid fission of the strained lactone ring in this compound. In an attempt to determine the equilibrium position, both lactones (I) and (III) were treated at room temperature with base in a non-hydrolytic medium, 15% methanolic potassium hydroxide. Both experiments gave dehydroanhydropicropodophyllin[1] (IV) as colourless crystals (50% yield; m.p. 278°) from a yellow solution; the compound was characterised by u.v., i.r., and ^{1}H n.m.r. spectroscopy. The colour which developed probably arises from the extensively conjugated base (II); loss of hydride ion from this, or decomposition of the peroxide formed from it by oxygen capture,[2] are possible reaction mechanisms.



Ar=3,4,5-trimethoxyphenyl

This reaction links the apo-series with naturally occurring arylnaphthalenes of recent interest[3] and, in view of a report[4] of their natural co-occurrence with (III), it could have biogenetic significance.

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