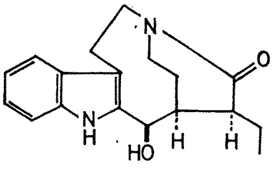
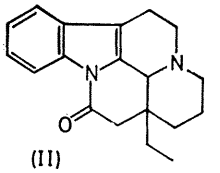
Novel Rearrangement of an Intermediate in Strychnos-type Alkaloid Synthesis

By JOHN HARLEY-MASON* and C. G. TAYLOR
(*University Chemical Laboratory, Lensfield Road, Cambridge,* CB2 1EW)

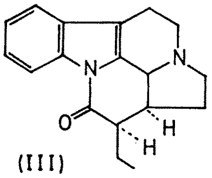
Summary A novel rearrangement of a tetracyclic hydroxy-lactam containing a nine-membered ring to give a new pentacyclic lactam by transannular collapse is described.



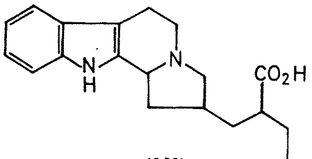
(I)



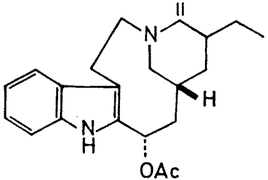
(II)



(III)



(IV)



(V)

THE readily available hydroxy-lactam (I) is a key intermediate in the total synthesis of Strychnos-type alkaloids.[1] Treatment with cold acetic anhydride–pyridine mixture gives the expected *O*-acetate;[1] however, treatment with cold trifluoroacetic anhydride leads to a wholly different reaction. The product, a tertiary base readily forming a methiodide, has a composition corresponding to loss of a molecule of water. Its u.v. spectrum and the carbonyl frequency in the i.r. spectrum are identical with those of eburnamonine (II). The product is, therefore, formulated as (III), and the mass-spectral fragmentation pattern is consistent with this formulation.

We envisage the transformation (I) → (III) as commencing by formation of the *O*-trifluoroacetate. This good leaving group then initiates transannular reaction with the lactam N(*b*), expelling an acylium ion which then recyclises to a new lactam by reaction with N(a). This new reaction is of interest in that it is a formal *reversal* of the acetic anhydride-induced conversion of the amino-acid (IV) to the hydroxy-lactam (V) used earlier[2] for total synthesis in the cleavamine field, in which a nine-membered ring is established.

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[1] B. A. Dadson and J. Harley-Mason, *Chem. Comm.*, 1969, 665.

[2] J. Harley-Mason and Atta-ur-Rahman, *Chem. Comm.*, 1967, 1048.