The Rearrangement of 20-Substituted Bisnorallocholanes and Derivatives

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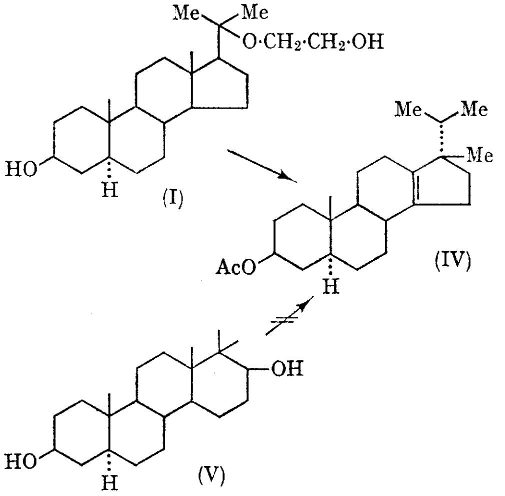
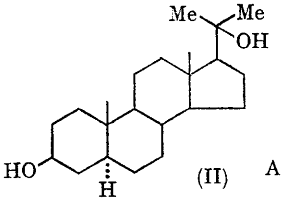
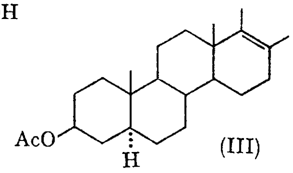
The action of acetic acid containing a catalytic amount of iodine on 20-(2-hydroxyethoxy)-bisnorallocholan-3β-ol (I) gave, after chromatography, only one (*ca.*, 80% yield) rearranged product, with the empirical formula $C_{22}H_{36}O$, which was identical in all respects (m.p., specific rotation, infrared comparison, and R_F values) with the product obtained under the same conditions by the dehydration of bisnorallocholane-3β,20-diol (II) and formulated as (III) by Uskokovic *et al.*[1]

We sought further evidence for the postulated structure (III) by n.m.r. examination of the rearranged product. Structure (III) would require the presence of two vinyl methyl groups near δ 1·7. The n.m.r. spectrum of the rearranged product showed the presence of four methyl groups between the region of δ 0·75 and δ 0·99, two of them being secondary and attributable to an isopropyl group, and the remaining two being tertiary. There was no indication of the presence of vinyl methyl groups. The postulated D-homo-system (III) is consequently untenable and we suggest the structure (IV), an 18-nor-17α-isopropyl-17β-methyl-13-androstene system, which may be envisaged as formed by a hydride shift from C-17 to the initially formed C-20 carbonium ion, followed by a 1,2-shift of the C-18 methyl group to C-17, and loss of a proton at C-14. The n.m.r. signals at δ 0·75 (doublet, $J = 7{\cdot}5$ c./sec.) and δ 0·85 (doublet, $J = 6{\cdot}5$ c./sec.) are attributable to the methyl protons on the isopropyl group at C-17. The remaining singlets at δ 0·81 and δ 0·99 are assigned to the C-19 and C-17 methyl protons, respectively. Structure (IV) was further substantiated by mass spectral analysis. The spectrum exhibited the proper molecular ion peak at *m*/e 316, loss of methyl (*m/e* 301) and an intense fragment at *m/e* 273 due to the loss of 43 mass units (C_3H_7) attributable to the removal of the isopropyl group at C-17.[2]





(II)



(III)

Still unexplained is the reported rearrangement of 17α,17β-dimethyl-D-homoandrostane-3β,17β-diol (V) and (II) to yield the same product. In our hands identical treatment of (II) and (V) yield different products. The nature of the products obtained from (V) is currently under investigation.

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[1] M. Uskokovic, M. Gut, and R. I. Dorfman, *J. Amer. Chem. Soc.*, 1960, **82**, 3668.

[2] Recently similar rearrangements at C-17 of steroids have been described by H. Laurent, H. Miller, and R. Wiechert, *Chem. Ber.*, 1966, **99**, 3836, and B. Krieger and E. Kaspar, *ibid.*, 1967, **100**, 1169.