Reactions of 5α-Cholest-2-ene with Iodine and Silver Salts

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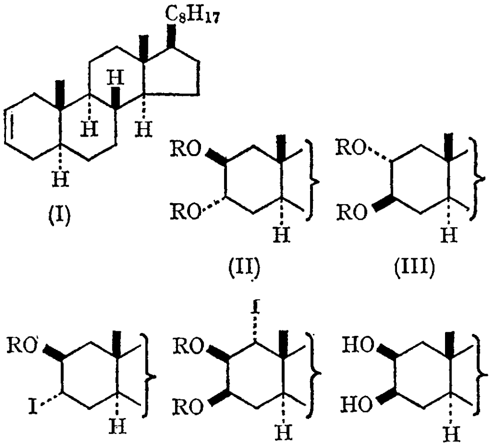
WHILE investigating methods for converting steroid olefins into vicinal diols we have studied the reactions of 5α-cholest-2-ene (I) with iodine and three silver salts in dry benzene (Prévost conditions[1]) at 80° and 20°. Using silver benzoate the expected diaxial dibenzoate (II; R = Bz) was obtained, together with the diequatorial isomer (III; R = Bz) in approximate ratios of 2 : 1 at 80° and 9 : 1 at 20°. With silver 3,5-dinitrobenzoate similar esters [II and III; R = 3,5-$(NO_2)_2C_6H_3$·CO] were formed, and from the reaction at 20° the intermediate 3α-iodo-2β-ester (IV) was isolated in moderate yield. Silver *p*-chlorobenzoate gave a surprising result: at 80° the normal, diaxial diester (2; R = *p*-Cl·C_6H_4·CO) was accompanied by an iodo-diester, and at 20° the latter was the sole product isolated

(30% yield). Spectroscopic investigation and chemical transformations led to structure (VI) for this iodo-diester, but the mechanism of its formation has not been established.



(I)

(II)

(III)

(IV) R=3,5-dinitrobenzoyl

(V) R=CF_3CO

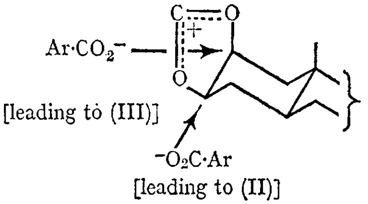
(VI) R=*p*-chlorobenzoyl

(VII)

With the object of isolating the intermediate (a 3α-iodo-2β-ester) more readily, 5α-cholest-2-ene was treated with iodine and silver trifluoroacetate in methylene chloride at 20°. The product, obtained in 72% yield, was shown to be 3α-iodo-5α-cholestan-2β-yl trifluoroacetate (V): the corresponding 3α-bromo-compound was also prepared, but in lower yield. Reactions of the iodo-trifluoroacetate provided convenient routes to 5α-cholestan-2β-ol and 2β, 3β-epoxy-5α-cholestane.

Treatment of the iodo-trifluoroacetate with silver trifluoroacetate at 100°, followed by hydrolysis with alkali afforded 5α-cholestane-2β,3β-diol (VII), the overall yield from 5α-cholest-2-ene being 50%. This diol has been obtained (50%,[2] 65%[3]) directly from 5α-cholest-2-ene by reaction with iodine and silver acetate in moist acetic acid (Woodward's method[4]). Further investigation showed that the direct method is considerably improved (to 81% yield) by conducting the reaction for 12 hours at 20° under nitrogen. (The conventional procedure involves heating for some time after the initial reaction period.)

It is believed that the reactions with the silver salts of aromatic acids described above proceed by ring-opening of dioxolenium cations (VIII). If this is so the opening, while giving mainly diaxial products, is by no means stereospecific, especially at 80°. Comparison of the results with the recent findings of King and Allbutt[5] suggests that the degree of specificity is influenced both by structural features and by experimental conditions.



(VIII)

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