

PREPARATION OF ALLOPREGN-14-ENE-3 β , 20 α -DIOL

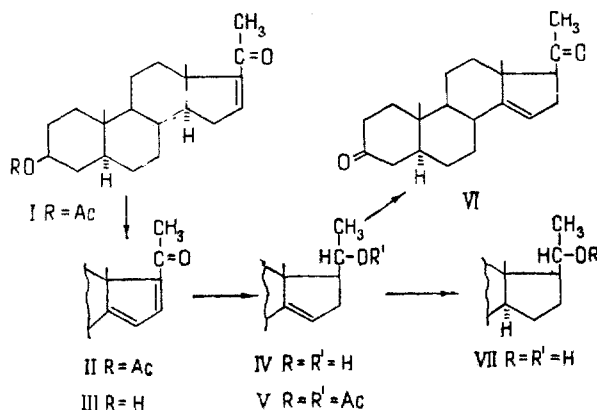
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3 β -Hydroxyprenenes with a double bond at C₁₄ can be used as the starting materials for syntheses of steroid aglycones. One of the methods of obtaining compounds of this type is the reduction of 14, 16-dienes with sodium in propanol or with lithium in liquid ammonia [1].

In order to obtain allopregnane-14, 16-diene, we subjected 3 β -hydroxyallopregn-16-en-20-one acetate (I) to allyl bromination with N-bromosuccinimide in carbon tetrachloride solution [2]. The subsequent splitting off of hydrogen bromide was carried out by boiling the bromide with a solution of sodium iodide in acetone [3]. The crude diene was chromatographed through a column of silica gel. The column was eluted with a mixture of benzene and ethyl acetate in a ratio of 30:1. The first fractions of eluate contained the unchanged allopregn-16-ene acetate (I) and the later fractions the diene (II), which had mp 175-178° C (from acetone-methanol); $[\alpha]_D^{20} + 416.0 \pm 2.5^\circ$ (c 1.70; chloroform). UV spectrum; $\lambda_{\text{max}}^{\text{C}_2\text{H}_5\text{OH}}$ 310 m μ (log ϵ 4.15) [4]. The yield of II taking into account the allopregn-16-ene acetate (I) recovered was 40-45%. Saponification of the acetate (II) with potassium hydroxide in tertiary butyl alcohol [4] led to 3 β -hydroxyallopregnane-14, 16-dien-20-one (III), with mp 159-160.5° C (from ethyl acetate), $[\alpha]_D^{20} + 439.5 \pm 2.5^\circ$ (c 1.25; chloroform). UV spectrum; $\lambda_{\text{max}}^{\text{C}_2\text{H}_5\text{OH}}$ 310 m μ (log ϵ 4.2).

Reduction of II with sodium in liquid propanol gave allopregn-14-ene-3 β , 20 α -diol (IV) with mp 184-185.5° C (from ethyl acetate); $[\alpha]_D^{18} + 29.4 \pm 1.5^\circ$ (c 0.76; chloroform). The IR spectrum lacked absorption in the region of ester and CO groups. The yield of crude diol (IV) was 40-45%. Acetylation of IV with acetic anhydride in pyridine yielded the diacetate V with mp 153-155° C (from acetone); $[\alpha]_D^{20} + 15.2 \pm 3.0^\circ$ (c 0.99; chloroform).



In compound IV the double bond at C₁₄ and the β -configuration of the side-chain at C₁₇ are shown by the oxidation of IV with chromic anhydride to allopregn-14-ene-3,20-dione (VI) [1], with mp 188-190° C (from acetone); $[\alpha]_D^{29} + 75.8 \pm 3.5^\circ$ (c 0.53; chloroform). The negative increment of the difference in the molecular rotations of the diacetate V and the diol IV ($[M]_D$ for the diacetate V +61.2°; $[M]_D$ for the diol IV +93.6°; $\Delta[M]_D -32.4^\circ$) shows that the hydroxy group at C₂₀ in the pregnenediol IV has the α configuration [1, 5]. An additional confirmation of this is the conversion of IV on hydrogenation over Pt into allopregnane-3 β , 20 α -diol (VII) [5] with mp 215-216° C, $[\alpha]_D^{18} + 21.4 \pm 4.3^\circ$ (c 0.72; chloroform).

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