HYDRATION REACTION OF 17-ETHYNYL SUBSTITUTED 19-NORSTEROIDS

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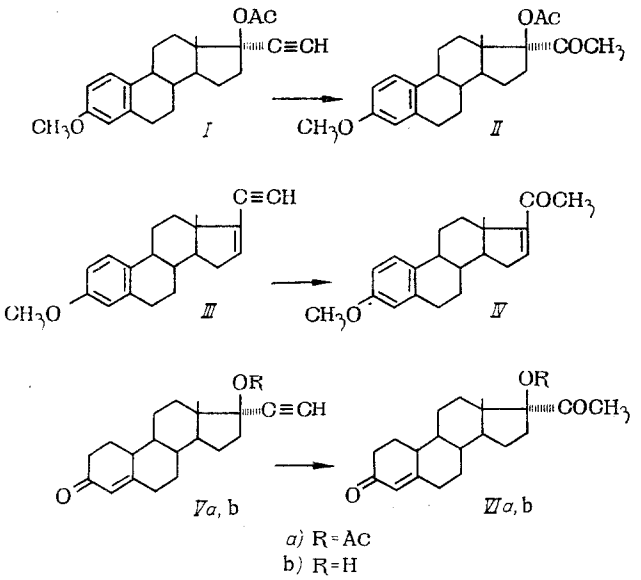
The hydration reaction of 17-ethynyl substituted steroids in the presence of divalent mercury is of interest as a method of obtaining 17-acetyl substituted steroids from 17-ketosteroids. Different variants of this reaction have been described in the literature one of which is the hydration of 17α-ethynyl substituted 17β-hydroxy(acetoxy)androstane in the presence of mercury and Dowex-50 cation exchange resin [1, 2].

We have used this reaction in a series of 19-norsteroids and have obtained the corresponding 17-acetyl substituted derivatives. Thus from mestranol acetate (I), 3-methoxy-17a-acetoxy-19-nor-17-isopregna-1,3,5(10)-trien-20-one (II) was obtained in 80% yield and 3-methoxy-19-norpregna-1,3,5(10),16-tetraen-20-one (IV) was obtained from 3-methoxy-17-ethnylestra-1,3,5-(10),16-tetraene in 73% yield. Hydration of norethisterone acetate (Va) in the presence of Dowex-50 (H form) proceeded readily and 17β-acetoxy-19-nor-17-isoprogesterone was isolated in 71% yield. This compound may be converted by known methods [3] into 19-norprogesterone which possesses high gestogenic activity [4]. 17β-Hydroxy-19-nor-17-isoprogesterone (VIb) was isolated from norethisterone (Vb) in a similar manner. There was an absorption band for hydroxyl group at 3340 cm^{-1} in the IR spectrum of compound (VIb) and for two carbonyl groups at 1708 (CO) and 1650 cm^{-1} (C=CCO). Signals for three methyl protons at 0.9 ppm (CH_3) and 2.12 ppm ($COCH_3$) were observed in the NMR spectrum as well as a signal for a vinyl proton at 5.64 ppm. In contrast to (VIa) the alcohol (VIb) was unstable, attempts to recrystallize (VIb) from methanol led to partial D-homoisomerization: in the NMR spectrum a signal for CH_3 group protons appeared at 1.28 ppm in place of the signal for protons at 2.12 ppm.



a) R=Ac
b) R=H

EXPERIMENTAL

3-Methoxy-17β-acetoxy-19-nor-17-isopregna-1,3,5(10)-trien-20-one (II). A solution of (I) (0.5 g) and mercuric acetate (0.13 g) in methanol (25 ml) and water (4 ml) was boiled for 6 h with Dowex-50 W-4 (H form) resin (0.4 g). The solid was filtered off and washed on the filter with chloroform. The chloroform solution was washed with water and evaporated in vacuum. The residue was recrystallized from ether and (II) (0.42 g) of mp 157-158°C was obtained; according to literature data [3] mp 159-161°C.

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3-Methoxy-19-norpregna-1,3,5(10),16-tetran-20-one (IV) was obtained as in the previous experiment from (III) (350 mg) yielding 270 mg mp 192-193°C; according to literature data [5] mp 192-193°C.

19-Nor-17-isopregnene-4-en-17β-ol-3,20-dione Acetate (VIa). A solution of 17α-ethynyl-esta-4-en-1β-ol-3-one acetate (Va) (1 g) and mercuric acetate (0.26 g) in methanol (40 ml) and water (7.5 ml) was boiled for 1½ h with Dowex-50 resin (0.5 g). The resin was filtered off and the solvent distilled off in vacuum. The residue was dissolved in methylene chloride, the obtained solution was washed with water, dried over calcined sodium sulfate, and evaporated in vacuum. The residue was crystallized from ether and (VIa) (0.75 g) of mp 172-173°C (from ethanol) was obtained; according to literature data [3] mp 173-174°C.

19-Nor-17-isopregnene-4-en-17β-ol-3,20-dione (VIb) was obtained in the same manner as the acetate (VIa) from 17α-ethynylestra-4-en-17β-ol-3-one (Vb) (1 g). Yield was 0.73 g mp 160-161°C; mass spectrum, M^+ 316; IR spectrum (cm^{-1}): 3340 (OH), 1708 (CO), 1750 (C=CO), 1610 (C=C); NMR spectrum in carbon tetrachloride (δ, ppm): 0.9 (CH_3), 2.12 ($COCH_3$), 5.64 (=CH).

LITERATURE CITED

1. G. Amiard, M. Legrand, J. Mathieu, et al., Bull. Soc. Chim. Fr., 2417 (1961).
2. A. A. Akhrem, T. K. Ustynyuk, and I. I. Voznesenskaya, Izv. Akad. Nauk SSSR, Ser. Khim., 639 (1973).
3. J. S. Mills, H. J. Ringold, and C. Djerassi, J. Am. Chem. Soc., 80, 6118 (1958).
4. L. Fieser and M. Fieser, Steroids, Reinhold, New York (1959) [Russian translation: Moscow (1964), p. 605].
5. D. Burn and V. Petrov, J. Chem. Soc., 364 (1962).

PURIFICATION OF EFFLUENTS CONTAINING SURFACE-ACTIVE SUBSTANCES BY THE PROCESS OF RADIATION FOAM QUENCHING

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A specific type of pollution in effluents has emerged owing to the wide distribution in industry and living conditions of synthetic surface-active substances (SSAS).

Because of this foam is generated on purifying effluents in installations for biochemical purification. Foam, passing out from installations into a reservoir or as residual amounts of SSAS in purified water, disrupts the oxygen regimen of rivers and reservoirs.

It is practically impossible to prevent the appearance of foam in purification installations. Consequently the need to combat this phenomenon is increasing, either to concentrate SAS or to break them down.

Effluents from some undertakings in drug manufacture may contain large quantities of SAS reaching 200-250 mg/liter.

The possibility of anion-active and nonionogenic SSAS being fed into installations for biological purification is provided for in building norms and rules. The overall concentration of them must not exceed 20 mg/liter. Thus all effluents with a high concentration of SSAS need to be subjected to local purification before passing into an installation for biochemical purification.

Industrial effluents may be purified from SAS by using certain physicochemical procedures [1, 2].

At the present time the adsorption method, viz., the sorption of SAS on aluminum hydroxide, is the most widespread. However, in the sorption purification process a significant

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