Patented Aug. 22, 1944

2,356,596

UNITED STATES PATENT OFFICE

2,356,596

ELECTROLYTIC PRODUCTION OF UNSATURATED KETOLS

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No Drawing. Application March 9, 1940, Serial No. 323,139. In Hungary August 31, 1939

3 Claims. (Cl. 204—75)

According to the known process for the production of unsaturated ketols of the cyclopentane-polyhydro-phenanthrene series the final product is obtained by several steps, through several intermediate products, using diketones as starting material. This process is complicated and producing only an insufficient output. The biochemical process of Mamoli and Vercellone (Ber. d. D. Chem. Ges. 70, 470, 1937) shows the drawback of the necessary use of large quantities of materials and needs therefore vessels of considerable volume.

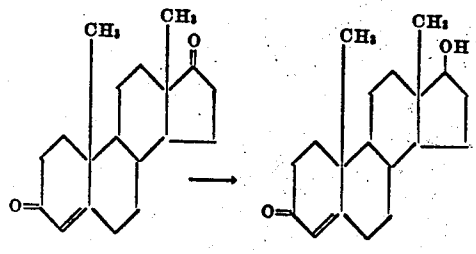
By the process according to the invention unsaturated ketols of the cyclopentane-polyhydro-phenanthrene series can be obtained in a single step by subjecting the unsaturated polyketones of that series to reduction by electrolysis. A considerable advantage therein is the quick and easily regulated electrochemical process and the simplicity of the separation of the products.

The electrolysis is carried out by the use of a diaphragm and preferably with ethyl alcohol or any organic solvent miscible with water. Further it is advantageous to use in the electrolysis the maximum quantity of electric current as calculated theoretically.

If non-electrolyte solvents are used, an electrolyte is to be dissolved therein. For this purpose sodium acetate in ethyl alcohol, glacial acetic acid in hydrochloric acid and the like can be used. The cathode consists preferably of lead, nickel, copper, carbon or platinum. The temperature of the cathode compartment is kept during the electrolysis preferably between 40 to 80° C. and the material therein is stirred constantly. The surface density of current on the cathode is preferably 1 to 4 amp./dm.^{2}.

If one of the diketones of the said series have been used as starting material for the electrolysis only one of their keto-groups becomes reduced, the existing unsaturated junction of the compound remaining undisturbed.

The following formulae show the process in question:



Example

2.5 grammes of Δ^4-androstendion-(3,17) are dissolved in a 5% solution of sodium acetate and subjected to electrolysis between a cathode of lead arranged in a diaphragm of clay and a sheet shaped anode of lead placed in a 5% solution of sodium acetate. The temperature of the cathode cell is kept between 55 and 60° C. and the catholyte is stirred during the electrolysis. The surface density of the current amounts 2 to 3 amp./dm.^{2} on the cathode, the three- to fourfold quantity of current passing the cell during the electrolysis as calculated theoretically. After completion of the electrolysis the catholyte is evaporated down to a volume of 30 to 40 cm.^{3}, the remainder is diluted with water to the threefold volume and left to stand for several hours. The crystalline precipitate is filtered, several times washed with water and dried. The dry material is dissolved in 20 cm.^{3} of hot methanol and left overnight. The small quantity of testosterone C (m. p. 222° C.), crystallizing out from the solution is separated by filtration, the solution is evaporated down to a small volume and the crystallized testosterone T is collected as main product, washed with a small quantity of ether and dried. A further purification of the product can be carried out by re-crystallization from hot benzine. The product shows a melting point of 153° C.

If Δ^4-pregnendion-3,20 has been used at the start a crystalline mixture of two stereoisomers of the Δ^4-pregnenol-20-on-3 is obtained and collected under the same conditions.

We claim:

1. The process for the production of unsaturated ketols of the cyclopentane-polyhydro-phenanthrene series by electrolytic reduction of the unsaturated polyketones of said series, which comprises dissolving an unsaturated polyketone of the group consisting of Δ^4-androstendone-3,17 and Δ^4-pregnendione-3,20 in an alcoholic solution of sodium acetate, subjecting the solution while stirring and at a temperature between 55 and 60° C. to cathodic electrolysis with a current density of two to three amperes per square decimeter, and separating out the product by crystallization.

2. Process for the production of unsaturated ketals of the cyclopentane-polyhydro-phenanthrene series by electrolytic reduction of unsaturated polyketones of that series in which Δ^4-androstendione-3,17 dissolved in a catholyte consisting of an alcoholic solution of sodium ace-

tate is electrolyzed in the stirred catholyte kept at 55–60° C., using clay diaphragm and lead electrodes in the process, electrolyzing by a current density of 2 to 3 amp./dm.^{2} and with three to fourfold the theoretical current, and collecting the crystallized testosterone produced.

3. Process for the production of unsaturated ketols of the cyclopentane-polyhydro-phenanthrene series by electrolytic reduction of unsaturated polyketones of that series, in which Δ^4-pregnendione-3,20 dissolved in a catholyte consisting of an alcoholic solution of sodium acetate is electrolyzed in the stirred catholyte kept at 55–60° C., using clay diaphragm and lead electrodes in the process, electrolyzing by a current density of 2 to 3 amp./dm.^{2} and with three to fourfold the theoretical current, and collecting the Δ^4-pregnenole-20-on-3 produced.

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