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PROCESS FOR THE PRODUCTION OF UNSATURATED KETONALCOHOLS OF THE CYCLOPENTANO - POLYHIDRO - PHENANTRENE SERIES

Andreas Krámli and László Vargha, Budapest, Hungary; vested in the Alien Property Custodian

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According to the known process for the production of unsaturated ketonalcohols of the cyclopentano - polyhidro - phenantrene series the final product is obtained by several steps, thorough several intermediate products, using diketones as starting material. This process shows the disadvantage to be complicated and to bring forth but an insufficient output. The biochemical process of Mamoli and Vercellone (Ber. d. D. Chem. Ges. 70, 470, 1937) shows the drawback of the necessitate use of large quantities of materials and needs therefore vessels of considerable volume.

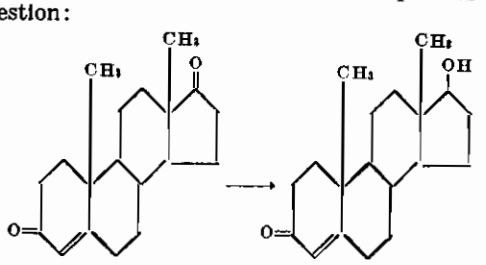
By the process according to the invention unsaturated ketonalkohols of the cyclopentano-polyhidro-phenantrene series can be obtained in a single step by subjecting the unsaturated polyketones of that series to reduction by electrolysis. A considerable advantage thereat is the quick and easily regulated electrochemical process and the simple way 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 multiple 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-room is kept during the electrolysis preferably between 40 to 80° C. and the material therein is permanently stirred. The surface density of current on the cathode is preferably 1 to 4 amp/dm².

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 present unsaturated junction of the compound remaining thereat 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 elektrolysis 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-room is kept between 55 and 60° C. and the catholite is stirred during the electrolysis. The surface density of the current amounts 2 to 3 amp/dm² on the cathode, the three- to fourfold quantity of current passing the cell during the electrolysis as calcluated theoretically. After ending of the electrolysis the catholite is evaporated up to a volume of 30 to 40 cm³, the remainder is diluted with water to the threefold volume and left to stand for several hours. The crystalline solid fallen out is filtered, several times washed with water and dried. The dry material is dissolved in 20 cm³ 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 up 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 from Δ^4-pregnendion-3,20 has been started a crystalline mixture of two stereoizomeres of the Δ^4-pregnenal-20-on-3 is obtained and collected under the same conditions.

ANDREAS KRÁMLI.
LÁSZLÓ VARGHA.