PERIODATE OXIDATION OF STEROIDAL Δ^4-3-KETONES

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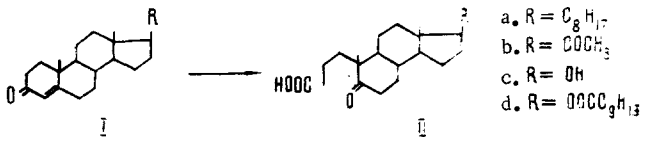
Steroidal seco acids of the type of Windaus's keto acid (IIa) [1] are of interest as the starting material for the synthesis of heterocyclic steroids [2]. They are produced by the oxidation of the corresponding Δ^4-3-ketones (I):



However, the known methods [2] of performing this oxidation have a number of disadvantages. In the literature [3] the preparation of the acid (IIa) by the use of a periodate-permanganate oxidizing agent has been described [4]. In the present work we have shown the possibility of using this simple and convenient method for oxidizing other Δ^4-3-ketones (Ib-d). With stirring, a solution of 7 g of potassium carbonate in 150 ml of water, 200 ml of a solution of 30 g of sodium metaperiodate in 400 ml of water, and 3 ml of an 0.8% solution of $KMnO_4$ were added successively to a solution of 10 g of progesterone (Ib) in 600 ml of the water – tert-butanol azeotrope. The remainder of the metaperiodate solution was added in small portions over 1 h, a faintly pink color of the reaction mixture being maintained by the periodic addition of $KMnO_4$ solution. Then the mixture was left overnight, and it was acidified with H_2SO_4 and extracted with ether. The extract was washed with sodium bisulfite and with water and was dried, and the solvent was driven off. This gave 6.66 g (62.6%) of compound (IIb) with mp 169-170°C (from acetone). Literature data [5]: mp 168-170°C. The similar oxidation of 3 g of testosterone (Ic) gave 1.82 g (54.9%) of compound (II) with mp 199-200°C (from acetone). Literature [6]: mp 200-202°C. In a similar manner, 10 g of ester (Id) was oxidized to give 8.1 g of compound (IId) in the form of a faintly yellowish oil, which was hydrolyzed with KOH in boiling methanol, after which the mixture was diluted with water, acidified with H_2SO_4, and extracted first with hexane and then with chloroform. The hexane extract yielded 3.45 g of capric acid. The chloroform extract yielded 2.35 g [32.65%, calculated on the ester (Id)] of the keto acid (IIc).

LITERATURE CITED

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