Oxidation of Hydroxy-steroids

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WE report the first example of the use of alkynylamines1 for the oxidation of the hydroxy-group in steroids.2 This new procedure involves the acid-catalysed reaction of NNdiethylaminoprop-1-yne with dimethyl sulphoxide and can be illustrated by the oxidation of testosterone and 11hydroxyprogesterone.

The oxidations were conducted by stirring a mixture of the appropriate hydroxy-steroid (5 mmole), Me₂SO (5 ml.), NN-diethylaminoprop-1-yne (13.5 mmole), and dry benzene (3 ml.). A solution of 100% phosphoric acid (1.59 g.) in Me₂SC (1 ml.) was added to it dropwise and the reaction mixture was stirred at room temperature for 2 days. It

was then diluted with benzene (200 ml.), washed with 10% sodium hydrogen carbonate solution, and the organic phase was evaporated to dryness. The keto-steroid was isolated in 60% yield by chromatography of the residue over Silica Gel G. The physical constants of the keto-steroids thus obtained were in agreement with the literature values. Thus, the oxidation of testosterone and 11-hydroxyprogesterone furnished androst-4-ene-3,17-dione3 and 11-oxoprogesterone,4 respectively.

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