

Novel Synthesis of  $\Delta^{5(10)}$ -6-Oxo-steroids

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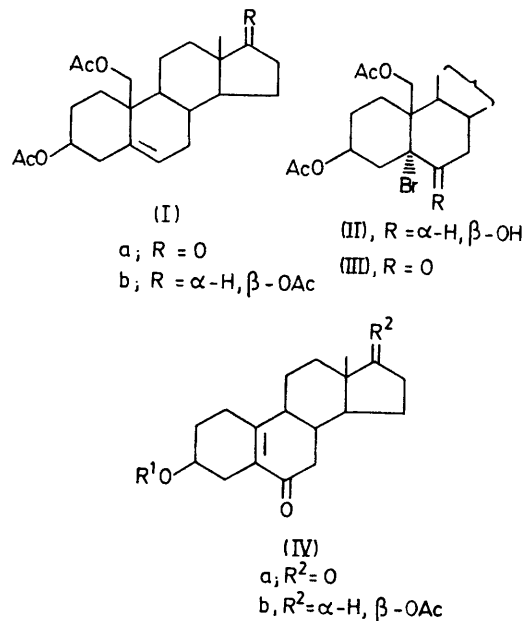
**Summary** A novel synthesis of estr-5(10)-en-6-ones is achieved by base-induced heterolytic fragmentation of 19-acetoxy-5 $\alpha$ -bromo-6-oxosteroids in good yield.

In our projected work connected with the possible fragmentation of steroids to prostanoids, we needed to prepare estr-5(10)-en-6-ones. After unsuccessful exploratory attempts to adapt the published procedures,<sup>1</sup> we developed a simple method for obtaining these intermediates by mild alkaline heterolytic fragmentation<sup>2</sup> of 19-acetoxy-5 $\alpha$ -bromo-6-oxo-steroids, resulting in simultaneous loss of the C(19)-acetoxy and 5 $\alpha$ -bromo-functions, apparently involving hydrolysis of the acetoxy group followed by deformylative-debromination.

Reactions of the 3 $\beta$ ,19-diacetate (Ia)<sup>3</sup> with *N*-bromosuccinimide in aqueous ether containing perchloric acid, led to the formation of the fairly unstable bromohydrin (II) which was easily oxidized with Jones reagent to the bromo-ketone (III). Treatment of the latter with boiling sodium carbonate solutions (20%) in methanol gave the required  $\Delta^{5(10)}$ -6-ketone (IVa, R<sup>1</sup>=H)<sup>†</sup> in good yield (35–40%), m.p. 220–222 °C;  $\nu_{\max}$  (CHCl<sub>3</sub>) 3300, 1725, 1650, and 1615 cm<sup>-1</sup>;  $\delta$ (CDCl<sub>3</sub>) 0.85 (s, 18-Me) and 3.45 (m, 3 $\alpha$ -H). The compound was further characterised by its acetate,<sup>†</sup> m.p. 148–149 °C;  $\nu_{\max}$  (Nujol) 1725, 1655, 1615, and 1240 cm<sup>-1</sup>;  $\delta$ (CDCl<sub>3</sub>) 0.85 (s, 18-Me), 2.1 (s, 3-acetate), and 3.45 (m, 3 $\alpha$ -H);  $\lambda_{\max}$  (EtOH) 250 nm ( $\epsilon$ , 13000).

The 3 $\beta$ ,17 $\beta$ , 19-triacetate (Ib) was similarly transformed into the  $\Delta^{5(10)}$ -6-one (IVb, R<sup>1</sup>=Ac).<sup>†</sup>

<sup>†</sup> The compounds gave satisfactory elemental analyses.



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<sup>2</sup> C. A. Grob, *Angew. Chem. Internat. Edn.*, 1969, **8**, 535.

<sup>3</sup> J. Kalvoda, H. Heusler, G. Ueberwasser, G. Anner, and A. Wettstein, *Helv. Chim. Acta.*, 1963, **46**, 1361.