

## Light-induced Formation of Seco-steroids

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**Summary** Acetone-sensitized irradiation of  $5\alpha$ -hydroxy- $\Delta^6$ -steroids affords the corresponding 5-oxo-5,6-seco-steroids in reasonable yields.

WE have previously investigated the photochemical behaviour of the  $5\alpha$ -hydroxy- $\Delta^6$ -steroids (3) and (4), obtained by photolytic oxidation of the readily available  $\Delta^5$ -steroids (1) and (2), respectively.<sup>1</sup>

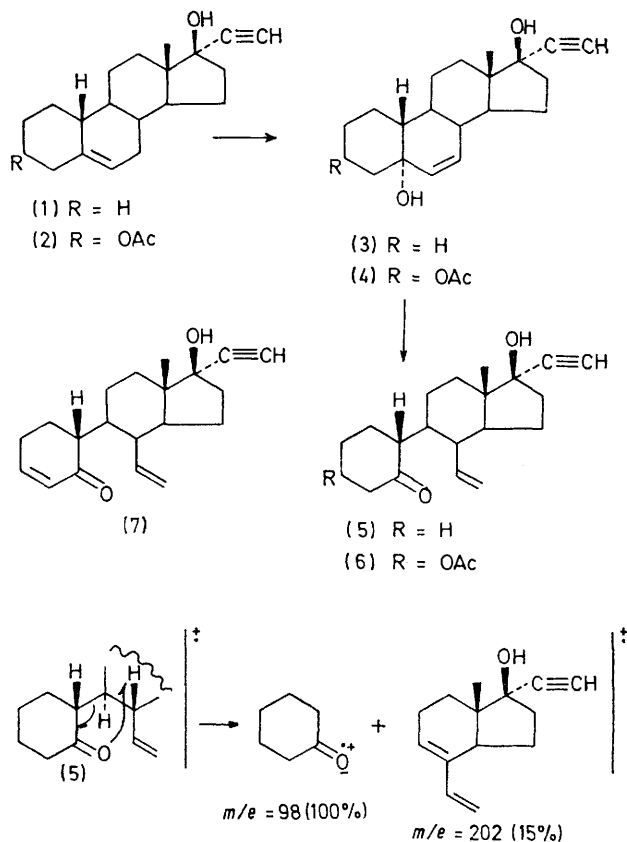
Irradiation of the  $5\alpha$ -hydroxy-compound (3) in acetone using a Philips HPW 125 mercury lamp afforded, after column chromatography, 30% of the seco-steroid (5) and the same amount of starting material (yields are not optimized). Structural evidence of compound (5) is mainly based on i.r. [ $\nu$  ( $\text{CCl}_4$ ) 1710 ( $\text{C}=\text{O}$ ), 3072, 1639, 913  $\text{cm}^{-1}$  ( $\text{HC}=\text{CH}_2$ )], n.m.r. [ $\delta$  (220 MHz,  $\text{CDCl}_3$ ) 4.86 (2H, AB part of ABX, 6-H), 5.25 (1H, m,  $J_{\text{trans}}$  18,  $J_{\text{cis}}$  9,  $J_{\text{gem}}$  2 Hz, 7-H)], and m.s. (parent  $m/e$  300, base 98) data.

The same irradiation procedure applied to the  $5\alpha$ -hydroxy-compound (4) yielded the corresponding seco-steroid (6) which in turn easily lost acetic acid to give (7) [ $\nu$  ( $\text{CCl}_4$ ) 1676 ( $\text{C}=\text{O}$ ), 3070, 1639, 911  $\text{cm}^{-1}$  ( $\text{HC}=\text{CH}_2$ );  $\delta$  (60 MHz,  $\text{CDCl}_3$ ) 5.18 (3H, m, 6- and 7-H), 6.00 (1H, dt,  $J_1$  10,  $J_2$  1.5 Hz, 4-H), 6.91 (1H, m, 3-H)].

This type of rearrangement did not take place with solvents other than acetone (*e.g.* tetrahydrofuran or benzene) with or without a suitable sensitizer; a low-pressure mercury lamp was also ineffective. These findings might indicate that in this conversion an acetone-induced proton shift is involved which in turn initiates a subsequent rearrangement to the seco-steroids.

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<sup>1</sup> N. P. Van Vliet and J. A. M. Peters, U.S.P. 3,708,511/1973.



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