

The Photochemical Rearrangement of Benzylenol Ethers of Δ^4 -3-Oxo-steroids

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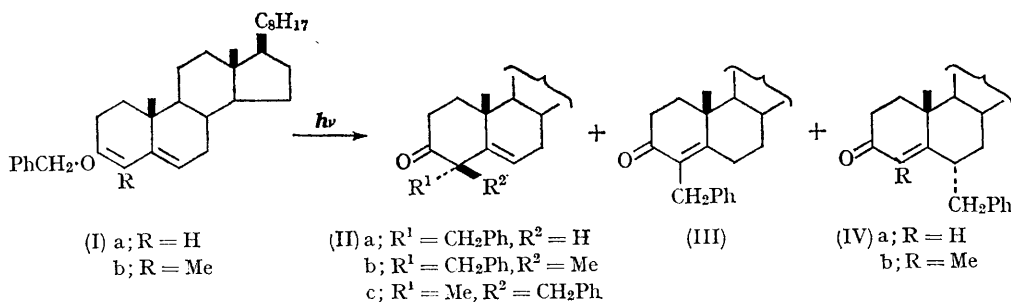
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It has recently been reported² that arylmethyl vinyl ethers undergo a peroxide-induced rearrangement to give β -arypropionaldehydes *via* a free-radical chain mechanism. We now report that benzylenol ethers of Δ^4 -3-oxo-steroids undergo a similar rearrangement on irradiation with ultraviolet light.

Photolysis of cholest-4-en-3-one benzylenol ether (Ia) in cyclohexane gave a mixture of three ketones which could be separated on silica gel. The major product (23%) was shown to be 4 α -benzylcholest-5-ene-3-one (IIa). In addition, there was obtained 4-benzylcholest-4-en-3-one (III, 13%) and 6 α -benzylcholest-4-en-3-one (IVa, 10%). The assignment of the 4 α -benzyl configuration in (IIa)

follows from the absence of a signal at higher field than δ 0.70 in its p.m.r. spectrum.³ As seen below in (IIc) a 4 β -benzyl group causes a large shift to higher field of the C-19 methyl group. Since (IVa) was stable to alkali the 6 α -benzyl configuration can be assigned to this compound.

In a similar manner 4-methylcholest-4-en-3-one benzylenol ether (Ib) rearranged to give 4 α -benzyl-4 β -methylcholest-5-ene-3-one (IIb), 4 β -benzyl-4 α -methylcholest-5-ene-3-one (IIc) and 6 α -benzyl-4-methylcholest-4-en-3-one (IVb). The assignment of configuration at C-4 in (IIb) and (IIc) was readily made on the basis of their p.m.r. spectra. In (IIc) the C-19 methyl signal is at δ 0.13, being shielded by the aromatic ring, whereas in the



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² A. W. Burgstahler, L. K. Gibbons, and I. C. Nordin, *J. Chem. Soc.*, 1963, 4986.

³ The p.m.r. spectra were run in CDCl₃ using SiMe₄ as internal reference on a Varian A-60 spectrometer.

p.m.r. spectrum of (IIb) there is no signal at higher field than δ 0.68. In the p.m.r. spectrum of (IVb) the signal due to the methyl group at C-4 is a doublet (δ 1.89, J 2.3 c./sec.). Since detectable

homoallylic coupling in 4-methylcholest-4-en-3-ones is confined to compounds with a β -hydrogen at C-6,⁴ compound (IVb) must have the benzyl group in the α -configuration.

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⁴ C. W. Shoppee, F. P. Johnson, Ruth E. Lack, R. J. Rawson, and S. Sternhell, *J. Chem. Soc.*, 1965, 2476.