The Photoisomerisation of an 11-Oxo-olean-12-ene[1]

By B. W. FINUCANE and J. B. THOMSON*

(*Department of Chemistry, University College, Dublin 4, Ireland*)

THE photochemistry of triterpene ketones has received little attention.[2] We report the first† photolysis of a conjugated triterpene ketone and a new example of the few known reactions induced selectively from the π,π^* excited state of $\alpha\beta$-unsaturated ketones.[3]

Irradiation‡ of 11-oxo-olean-12-en-3β-yl acetate (I) in the $\pi \rightarrow \pi^*$ absorption band yields 15% (30% based on unrecovered starting material) of a non-ketonic product, m.p. 234—235°, $[\alpha]_D$ $+110°$ ($CHCl_3$); ν_{max} (KBr) 3440 (OH which resists acetylation), 1735, and 1245 cm.$^{-1}$ (OAc); τ 9·20—8·66 (7Me), 7·96 (OAc), 5·35 (m, 3-H), and 4·80 (s, 12-H). The molecular formula, $C_{32}H_{50}O_3$ (mass spectrum), and the spectroscopic data indicate that the photo-product is either the hexacyclic alcohol (III) or its 11,16-cyclo-isomer (*cf.* ref. 4). That the former structure is correct is shown by the rapid, quantitative formation, under mildly acidic conditions, of a partly conjugated triene (IV), m.p. 198—199°, $[\alpha]_D$ $-142°$ ($CHCl_3$); λ_{max} (MeOH) 265 nm. (ϵ 34,000); the n.m.r. spectrum of which shows only one olefinic proton (s, τ 3·89). Confirmation of the cyclobutanol structure was obtained by oxidative cleavage[4,5] of the photo-product with lead tetra-acetate to give 3β-acetoxy-11-oxo-olean-12-en-25-ol (II), m.p. 229—230°, $[\alpha]_D$ $+79°$ ($CHCl_3$); λ_{max} (MeOH) 248 nm.; τ 9·14—8·63 (7Me), 7·98 (OAc), 6·05 (s, 25-H_2), 5·48 (m, 3-H), and 4·36 (s, 12-H).

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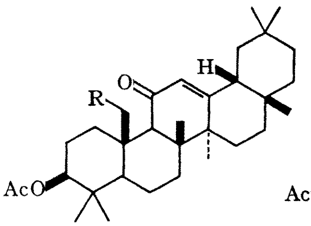
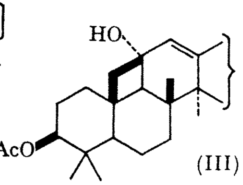
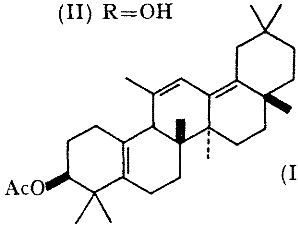


(I) R=H
(II) R=OH



(III)



(IV)

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† The photolactonisation of an iodo-amide containing, but not involving, the 11-oxo-12-ene chromophore has been described: L. Canonica, B. Danieli, P. Manitto, and G. Russo, *Gazzetta*, 1966, **96**, 843.

‡ A 0·003M-solution of (I) in dry, deoxygenated dioxan was irradiated (24 hr.) with an immersed NK 6/20 low-pressure mercury lamp (Quarzlampen, Hanau). The enone (I) is recovered quantitatively after prolonged $n \rightarrow \pi^*$ excitation.

[1] Previous paper in this series: R. Ó. Dorchaí, H. E. Rubalcava, J. B. Thomson, and B. Zeeh, *Tetrahedron*, 1968, **24**, 5649.

[2] D. Arigoni, D. H. R. Barton, R. Bernasconi, C. Djerassi, J. S. Mills, and R. G. Wolff, *J. Chem. Soc.*, 1960, 1900; F. Kohen and R. Stevenson, *Chem. and Ind.*, 1966, 1844; J. Fried and J. W. Brown, *Tetrahedron Letters*, 1967, 925; N. Sugiyama, K. Yamada, and H. Aoyama, *Chem. Comm.*, 1968, 1254.

[3] *Cf.* J. A. Saboz, T. Iizuka, H. Wehrili, K. Schaffner, and O. Jeger, *Helv. Chim. Acta*, 1968, **51**, 1362.

[4] H. Wehrli, M. S. Heller, K. Schaffner, and O. Jeger, *Helv. Chim. Acta*, 1961, **44**, 2162; J. Iriarte, K. Schaffner, and O. Jeger, *ibid.*, 1963, **46**, 1599.

[5] M. L. Mihailović, M. Jakovljević, V. Trifunović, R. Vukov, and Z. Ceković, *Tetrahedron*, 1968, **24**, 6959.