

A Photochemical Reaction of 16-Oxo-oleanenes

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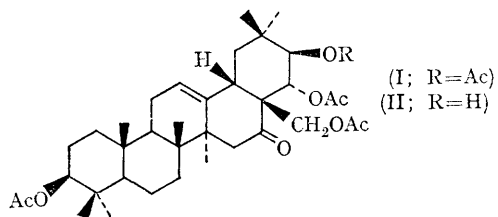
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PHOTOCHEMICAL reactions of cyclic ketones in solution have been much reported,¹ but similar studies on triterpenoid ketones are relatively few.² We report a photochemical cyclization of 16-oxo-oleanenes [(I) and (II)].²

A solution of (I) in methanol was irradiated with a 500 w high-pressure mercury lamp for three hours. Chromatography of the reaction mixture

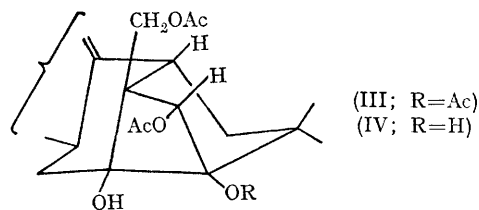
afforded (III) ($C_{38}H_{56}O_9$, m.p. 225°). The structure of (III) was confirmed by elemental analysis and physical data: mass spectrum peaks at 656 (M^+), 638 ($M - H_2O$), and 569 ($M - AcOH$); ν_{max} 3500 and 1163 cm^{-1} (OH group which has resisted acetylation and oxidation); τ 9.27—8.56 (7Me), 7.78—7.98 (4OAc), 5.54 and 6.03 [$C(28)H_2OAc$, AB q, J 10 c./sec.], 5.46

(1H m, C(3)HOAc), 4.88 (1H, C(22) HOAc), and 4.76 (1H, vinyl proton, m).



Irradiation of (II) under the same conditions gave the corresponding cyclization product (IV) ($C_{36}H_{54}O_8$, m.p. 227°), the structure of which was

also confirmed by elemental analysis, i.r., n.m.r., and mass spectra.



This is the first example of photochemical γ -hydrogen transfer of triterpenoid ketones.

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¹ O. L. Chapman, *Adv. Photochem.*, 1963, **1**, 323.

² D. Arigoni, D. H. Barton, R. Bernasconi, C. Djerassi, J. S. Mills, and R. E. Wolff, *Proc. Chem. Soc.*, 1959, 306; *J. Chem. Soc.*, 1960, 1900.

³ N. Sugiyama, K. Yamada, T. Sayama, and H. Aoyama, *J. Chem. Soc. Japan*, 1967, **88**, 1316; I. Yoshioka, T. Nishimura, A. Matsuda, and I. Kitagawa, *Tetrahedron Letters*, 1966, 5979; A. K. Barua and P. Chakrabarti, *Tetrahedron*, 1965, **21**, 381.