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PHOTOLYSIS OF VINYL BENZOATES[1]

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We wish to report the conversion of vinyl esters of benzoic acid to α-benzoylketones by irradiation with ultraviolet light. However cyclohexen-1-yl benzoate photolysis resulted in ring cleavage as well as in benzoyl migration.

The irradiations were performed in cyclohexane solution under nitrogen with a low pressure mercury immersion lamp (main emission line at 254 mμ). The progress of the reactions was followed spectroscopically by the disappearance of the 225-230 mμ absorption band of the starting material and the appearance of the 305-315 mμ band of the product. The α-benzoylketones were isolated in 10-30% yields, either through copper chelates or by chromatographic separations.

The photolysis of isopropenyl benzoate[2] for 1.5 hrs. yielded α-benzoylacetone. When cyclohexen-1-yl benzoate I [b.p. 120-122°/1 mm.; n_D^{20} , 1.5385],[3] prepared by refluxing benzoyl chloride and cyclohexanone in ligroin (b.p. 100-120°), was irradiated for 2 hrs., the product proved to be 1-benzoylhex-5-en-2-one [II, b.p. 123-

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[1] Presented in part at: (a) the 30th Meeting of Israeli Chem. Soc., Jerusalem, April 1962, Bull. Research Council Israel 11A, 43 (1962); (b) the 2nd International Symposium of the Chemistry of Natural Products, Prague, August 1962 (Abstract of Communications, p. 115).

[2] F.G. Young, F.C. Frostick, J.J. Sanderson and C.R. Hauser, J. Am. Chem. Soc. 72, 3635 (1950)

[3] A.N. Nesmeyanov and W.K. Kochetkov, C.A. 44, 7225^e (1950).

124°/1 mm.; n_D^{20}, 1.5845; $\lambda_{max.}$ 246 and 313.5 mμ (ϵ, 5700 and 13,800)].[4] The structure of II was indicated by its infrared and n.m.r. spectra [bands at 10.9μ and 10.08μ; two multiplets centered at τ = 4.85 and τ = 4.05 (assigned to a vinyl group) and a sharp signal at τ = 3.8 (assigned to a vinylic hydrogen of the enolic form of the β-diketone system)].[5] The structure of II was definitely established by its synthesis from methyl pent-4-enoate and acetophenone with sodium amide in ether. Cyclohexene ring cleavage was also observed when 6-methylcyclohexen-1-yl benzoate [III, b.p. 109-110°/0.4 mm.; n_D 1.5380] was irradiated for 6 hrs. Ester III was prepared from 2-methylcyclohexanone either by boiling with benzoyl chloride in ligroin (b.p. 100-120°) or with isopropenyl benzoate and sulfuric acid.[6,7] The isolated diketone was identified as 1-benzoyl-3-methyl-hex-5-en-2-one [IV, b.p. 102-104°/0.6 mm.; n_D^{20} 1.5612; $\lambda_{max.}$ 247 and 309 mμ (ϵ, 6000 and 16500)] by its infrared and n.m.r. spectra [(i) bands at 10.88 and 10.07μ and two multiplets centered at τ = 4.8 and τ = 4.05, indicating a vinyl group; (ii) a sharp signal at τ = 3.78 pointing to a vinylic proton of the enolic form of the β-diketone system; (iii) a doublet due to 3 protons of the secondary methyl group centered at τ = 9.0 ($\underline{J}$=6.5 c/s)]. The β-diketone IV was synthesized by sodium amide condensation of methyl 2-methyl-pent-4-enoate and acetophenone in ether.

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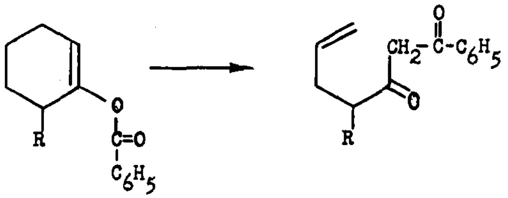
[4] Ultraviolet spectra were taken in ethanol; the infrared spectra and optical rotations were measured in chloroform and the n.m.r. spectra in deuteriochloroform. All new substances gave analytical results in accord with the assigned structures.

[5] This and all other α-benzoylketones mentioned in this paper exist mainly in one of their enolic forms whose structure is based on their n.m.r. spectra; to be published at a later date.

[6] The structure of III was determined by its n.m.r. spectrum, which showed signals due to 3 protons of a secondary methyl - doublet centered at τ = 8.96 ($\underline{J}$=6.5 c/s). The signal due to a vinylic methyl group of the alternate enol form was missing. It follows that the direction of enolization is strongly influenced by steric factors (cf. M.F. Hartshorn and E.R.H. Jones, J. Chem. Soc. 1962, 1312; B. Berkoz, E.P. Chavez and C. Djerassi, ibid. 1962, 1323).

[7] A vinyl-benzoate prepared previously has apparently the structure III [A.N. Nesmeyanov, I.F. Lutsenko and S.N. Ananchenko, C.A. 49, 3836 (1955)].



I R=H II R=H

III R=CH_3 IV R=CH_3

No ring cleavage was observed when steroidal vinyl benzoates were irradiated. Thus cholest-2-en-3-yl benzoate V[8] after 16 hrs. irradiation yielded 2-benzoyl-cholestan-3-one [VI, m.p. 120-122°; $[\alpha]_D$ -53.5°;[4] $\lambda_{max.}$ 245 and 313 mμ (ε, 5220 and 10,700)]. With diazomethane VI was converted to 2-benzoyl-3-methoxy-cholest-2-ene [VII, m.p. 130-131°; $[\alpha]_D$ +24.5°; $\lambda_{max.}$ 250 and 287 mμ (ε, 9700 and 4400)], which was reduced with sodium borohydride and then treated with hydrochloric acid[9] to yield the known 2-benzylidene-cholestan-3-one[10] [VIII; m.p. 122-123°; $[\alpha]_D$ -103.5^c $\lambda_{max.}$ 292.5 mμ (ε, 15,600)]. Androst-16-en-3β,17β-diol 3-acetate 17 benzoate [IX; m.p. 152-154°; $[\alpha]_D$ +40°; $\lambda_{max.}$ 231 mμ (ε, 12,750)], prepared from androstan-3β-ol-17-one acetate X by boiling with isopropenyl benzoate and sulfuric acid, was photolized for 2 hrs. to give 16-benzoylandrostan-3β-ol-17-one acetate [XI; m.p. 160-162°; $[\alpha]_D$ -64°; $\lambda_{max.}$ 246 and 314.5 mμ (ε, 8,400 and 11,500)]. The diketone XI was oxidized with chromic acid in acetic acid and then hydrolized to the known 3β-hydroxy-etioallobilianic acid XII,[11] thus establishing structure XI.

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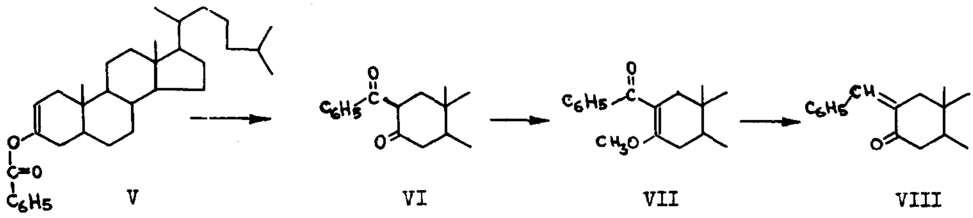
[8] L. Ruzicka and W.H. Fischer, Helv. Chim. Acta 19, 1371 (1936).

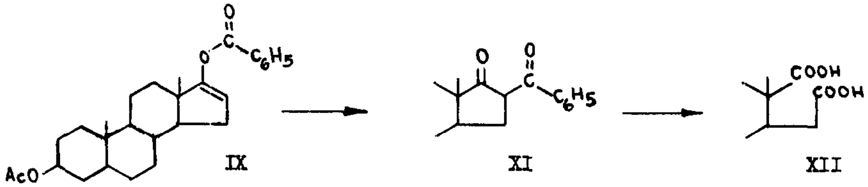
[9] Cf. R.D. Campbell and H.M. Gilow, J. Am. Chem. Soc. 82, 2389 (1960).

[10] M.W. Goldberg and H. Kirchensteiner, Helv. Chim. Acta 26, 288 (1943); D.H.R. Barton, A.J. Head and P.J. May, J. Chem. Soc. 1957, 935.

[11] H. Hirschmann, J. Biol. Chem. 150, 363 (1943).



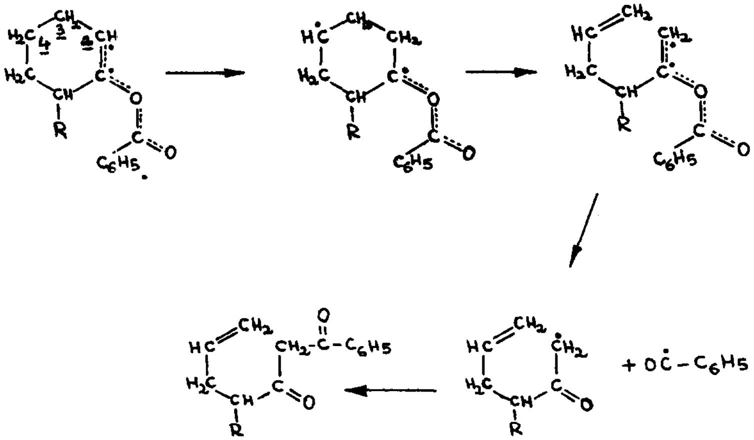
V VI VII VIII



IX XI XII

The light-induced rearrangements of vinylic benzoates involve two distinct processes. One is the formation of benzoyl radicals, which combine with the radical formed on the neighboring olefinic carbon. Analogous benzoyl and acetyl migration were recently described in the photolysis of phenyl esters.[12]

The accompanying process which occurs when I and III are irradiated involves a 1,3 hydrogen shift. A reasonable scheme for this transformation can be pictured as follows:



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[12] J. C. Anderson and C. B. Reese, Proc. Chem. Soc. (London) 217 (1960); H. Kobsa, J. Org. Chem. 27, 2293 (1962).

It is assumed that the excited state of the vinylic ester undergoes this hydrogen shift, hydrogen being abstracted from C_4, followed by the cleavage of the C_2-C_3 bond. Only then does the excited system dissociate into a radical pair, which on recombination gives rise to the α-benzoyl ketone.[13] In the cases where ring opening was not observed (V and IX), the primary excited state apparently decomposes directly into a radical pair, which then recombines to give the cyclic diketone.

Acyl and benzoyl migration of aliphatic vinylic esters are known to occur when the esters are treated with boron trifluoride[2] and also when they are pyrolyzed at 500°.[2,14]

It is important to note that the pyrolysis of cyclohen-1-yl-benzoates results in α-benzoyl-cyclohexanone[2,14] thus pointing to a major difference between the thermic and photochemical reaction of vinylic esters.

Work is in progress on the irradiation of vinyl acetates, where similar acyl migrations occur.

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[13] It should be stressed that no. II could be isolated when α-benzoylcyclohexanone was irradiated. This eliminates the possibility that a cyclic β-diketone is an intermediate in these ring cleavages.

[14] R. J. P. Allen, J. McGee and P. D. Ritchie, J. Chem. Soc. 1957, 4701 and references cited therein.