Photoisomerization of a Hydroxy-dienone to a Pyrone

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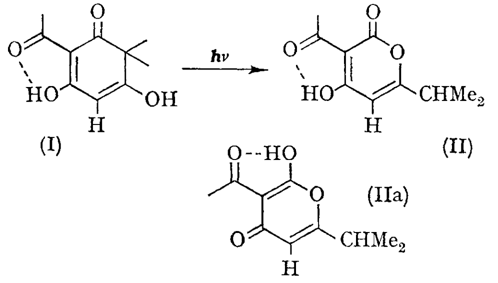
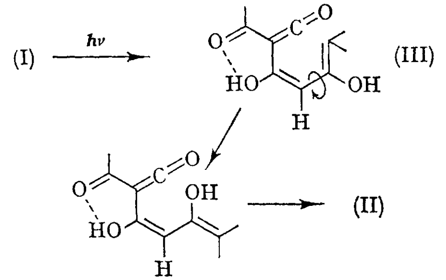
IN the preceding Communication, we described the photo-oxidation of the enolate anion of diacetylfilicinic acid, and presented evidence that the reaction proceeds *via* singlet oxygen. To extend the reaction to other substrates, we examined the photochemical behaviour of monoacetylfilicinic acid (I).[1] In alkaline solution (sodium methoxide–methanol), the monoanion of (I) underwent the same type of photochemical oxidation showing that the reaction is general. However, unlike diacetylfilicinic acid (V), which was photochemically inert in its un-ionized form, monoacetylfilicinic acid underwent a ready photoisomerization.



Irradiation of (I)† (0·15% solution) in ether or methanol through Pyrex using a Hanovia S 200 w lamp afforded, in over 80% yield, a crystalline isomer of (I), m.p. 55—56°, to which we assign the pyrone structure (II).‡ § The n.m.r. spectrum showed an acetyl methyl group (τ 7·48), a chelated hydroxyl proton (τ −6·9), a vinyl proton (τ 4·28) and an isopropyl group (doublet at τ 8·75, J = 7·0 c./sec., 6H and multiplet at τ 7·34, 1H). The u.v. and i.r. spectra of (II) strongly resembled those of dehydroacetic acid [(II), methyl in place of isopropyl].



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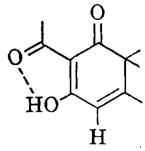
† Evidence that (I) has the tautomeric structure shown will be presented in the full paper.

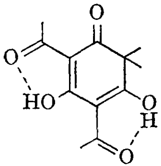
‡ All new compounds gave satisfactory analyses.

§ The choice between the α-pyrone structure shown and the γ-pyrone tautomer (IIa) is for the moment left open, since it is irrelevant to the reaction. The α-pyrone structure is used in the discussion because it most clearly shows the relationship between the reactant and product.

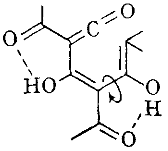
The reaction may proceed *via* a keten intermediate (III) which is trapped intramolecularly by the hydroxyl group.[2] Trapping must be remarkably efficient, since the reaction course was not deflected when methanol was the solvent.



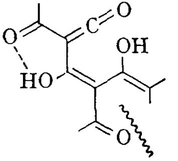
(IV)



(V)



(VI)



(VII)

The monomethyl ether (IV) prepared from (I) and diazomethane,[3] was photochemically inert in both neutral and alkaline solution, in a nitrogen or oxygen atmosphere. This result is consistent with the mechanisms already proposed for the photo-oxidation and photoisomerization.

Two possible reasons why monoacetylfilicinic acid undergoes photoisomerization whereas diacetylfilicinic acid (V) does not may be that rotation in the keten (VI) is inhibited by the hydrogen bond and would lead to a sterically strained conformer (VII). The scope and mechanism of this reaction is being further explored.

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[1] W. Riedl and K. H. Risse, *Annalen*, 1954, **585**, 209.

[2] For possibly related examples, see R. C. Cookson, A. G. Edwards, J. Hudec, and M. Kingsland, *Chem. Comm.*, 1965, 98.

[3] S. Forsen and M. Nilsson, *Acta Chem. Scand.*, 1959, **13**, 1383.