Photochemical Rearrangement of 4*H*-Pyran-4-ones to 2*H*-Pyran-2-ones

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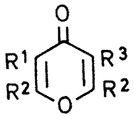
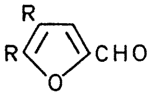
Summary Irradiation of 2,6-disubstituted-3,5-diphenyl-4*H*-pyran-4-ones (Ia,b) with a medium-pressure mercury lamp yielded 3,6-diphenyl-4,5-disubstituted-2*H*-pyran-2-ones (IVa,b).



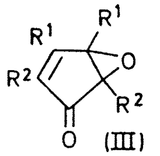
(I)

a; $R^1 = R^3 = Ph$, $R^2 = Me$
b; $R^1 = R^2 = R^3 = Ph$
c; $R^1 = R^3 = H$, $R^2 = Me$
d $R^1 = R^3 = H$, $R^2 = Ph$



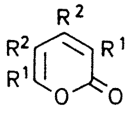
(II)

a; R = Me
b; R = Ph



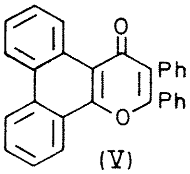
(III)

a; $R^1 = Ph$, $R^2 = H$
b, $R^1 = R^2 = Ph$



(IV)

a; $R^1 = Ph$, $R^2 = Me$
b; $R^1 = R^2 = Ph$



(V)

YATES and STILL[1] have found that u.v. irradiation of 2,6-dimethyl-4*H*-pyran-4-one (Ic) affords 4,5-dimethyl-2-furaldehyde (IIa) in 1% yield, and suggested that the mechanism of this photorearrangement initially proceeds by a route analogous to those of the photochemical transformations of cyclohexa-2,5-dienones.[2] Studies on the photolysis of 4,5-epoxycyclopent-2-enone derivatives (III)[3,4] have revealed that they undergo photoconversion into 2*H*-pyran-2-ones (IV), while (IIb) is formed *via* acid-catalysed rearrangement of (IIIa). Padwa and Hartman[3] have examined the photolysis of (Id) and were unable to detect the formation of (III) and (IV), obtaining only the photodimer.[5] We report the first example of photochemical transformation of 4*H*-pyran-4-ones into the isomeric 2*H*-pyran-2-ones.

A 0·3% solution of (Ib) in methylene chloride was irradiated at 30° under nitrogen by a 500 w medium-pressure mercury arc, the light being filtered through Pyrex. After irradiation for 5 h, (IVb) (m.p. 165—166°) and (V) (m.p. 240—241°)† were isolated in 42 and 7% yield, respectively. Photolysis of (Ia) in acetonitrile under the same conditions except for the use of a quartz filter‡ gave

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† Satisfactory elemental analyses were obtained for all new compounds.

‡ Irradiation of (Ia) filtered by Pyrex instead of quartz produced no reaction.

(IVa) (m.p. 155—156°) in 67% yield. The structure of (IVb) was established by comparison of its i.r. and n.m.r. spectra with those of an authentic sample prepared independently from the reaction of dimethylsulphonium β-phenylphenacylide with diphenylcyclopropenone.[6] The structure of (V) was decided on the basis of the following spectral data: M^+ m/e 398 [*cf.* m/e 400 for (Ib)] λ_{max} ($CHCl_3$) 264 (log ϵ 3·48), 293 (3·28), 337 (2·70), and 352 nm (2·48), pattern similar to that of phenanthrene; ν_{max} 1625 cm^{-1} (νC=O); δ ($CDCl_3$) 7·40 (s, 10H), 7·5—7·9 (m, 5H), 8·6—8·8 (m, 2H), and 10·3 (m, 1H).

The i r. spectrum of (IVa) exhibited strong bands at 1700 (νC=O), 1630, and 1550 cm^{-1} (νC=C), in agreement with its formulation as a 2*H*-pyran-2-one. The n.m.r. spectrum of (IVa) in $CDCl_3$ showed two singlets at δ 2·07 (3H) and 2·13 (3H) due to the methyl protons, while the methyl protons of (Ia) exhibited a singlet at δ 2·24 (6H). The mass spectrum of (IVa) showed intense peaks at m/e 248 ([M — CO]$^+$) and 143, the latter peak being formed by the further elimination of the benzoyl radical from the fragment [M — CO]$^+$.[7] This indicates the presence of the phenyl group at C-6 in (IV). The reaction of (IVa) with benzyne generated from diphenyliodinium-2-carboxylate gave 1,4-diphenyl-2,3-dimethylnaphthalene in 65% yield.

When (IVa) and (IVb) were heated with P_2S_5 in benzene, the corresponding 2*H*-pyran-2-thiones were formed, whose i.r. spectra contained no carbonyl stretching absorption but exhibited the strong band at 1270 cm^{-1} due to νC=S. This transformation of the carbonyl group into a thiocarbonyl group is characteristic of pyrone derivatives.[8]

The steric effect of substituents in (Ia) and (Ib) prevents formation of the photodimer,§ while the unhindered 4*H*-pyran-4-ones give exclusively the photodimer.[5] The formation of (IVa) from (Ia) suggests that the reaction proceeds by rearrangement of (I) to (III), followed by photochemical transformation to (IV), the photochemical rearrangement of (IIIb) to (IVb) having been reported.[4]¶

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§ Thin-layer chromatograms of the reaction mixtures showed no spots other than those of the identified photoproducts.

¶ Irradiation of (Ib) did not produce the transient pink coloration observed in the photolysis of (IIIb).[4]

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[7] M. M. Bursey and L. R. Dusold, *Chem. Comm.*, 1967, 712; M. M. Bursey, L. R. Dusold, and A. Padwa, *Tetrahedron Letters*, 1967, 2649.

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