Photochemical Formation of Hydroxycyclopentenones from Unsaturated 1,2-Diketones

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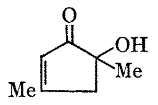
Summary Irradiation of some αβ-unsaturated 1,2-diketones leads to hydroxycyclopentenone derivatives in high yield.

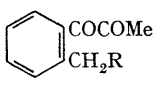
IT has been shown that excitation of the weak visible absorption band of suitably substituted 1,2-diketones leads to 2-hydroxycyclobutanone derivatives in a remarkably clean and efficient reaction.[1] We report here that suitably substituted unsaturated 1,2-diketones in which the double bond is conjugated to one of the carbonyl groups can lead to 5-hydroxycyclopent-2-enone derivatives in a similarly efficient process.

$Me_2C{:}CHCOCOMe$

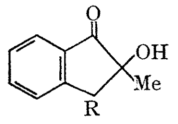
(I)



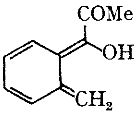
(II)



(III)a; R=H
b; R=Me



(IV)a; R=H
b; R=Me



(V)

When a pentane solution of 5-methylhex-4-ene-2,3-dione[2] (I) was irradiated under N_2 with sunlight, the characteristic yellow colour rapidly disappeared and removal of the solvent gave 3,5-dimethyl-5-hydroxycyclopent-2-enone (II) m.p. 48–49° in almost quantitative yield. Similarly the *o*-alkyl substituted aryl 1,2-diketones (IIIa,b) were likewise converted into the 2-hydroxyindanones (IVa, b) giving, in the second case, a mixture of the *cis*- and *trans*-isomers of the product. The reaction thus represents a particularly easy route to such compounds.

Since the related monoketones *o*-methyl- and *o*-benzylbenzophenone have been shown to undergo a reversible enolisation on irradiation[3] it seems relevant to report that the quantitative photocyclisation of (IIIa) to (IVa) in the presence of MeOD gives no deuterium incorporation in the 3-position of the product. Thus we conclude that photoenolisation to (V) is not competitive with the photocyclisation nor, the probable configuration of the enol being as shown and hence sterically unfavourable for an internal aldol condensation, is it probable that it is a precursor of the final product.

All new compounds gave satisfactory elemental analyses and had spectra in complete accord with their postulated structures.

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[2] G. Dupont, R. Dulou, and L. Audier, *Bull. Soc. chim. France*, 1955, 1708.

[3] N. C. Yang and C. Rivas, *J. Amer. Chem. Soc.*, 1961, **83**, 2213.