Norrish Type II Photoelimination of 1,2-Diketones

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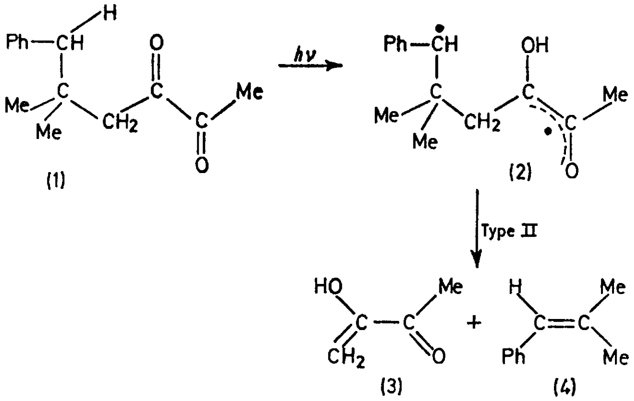
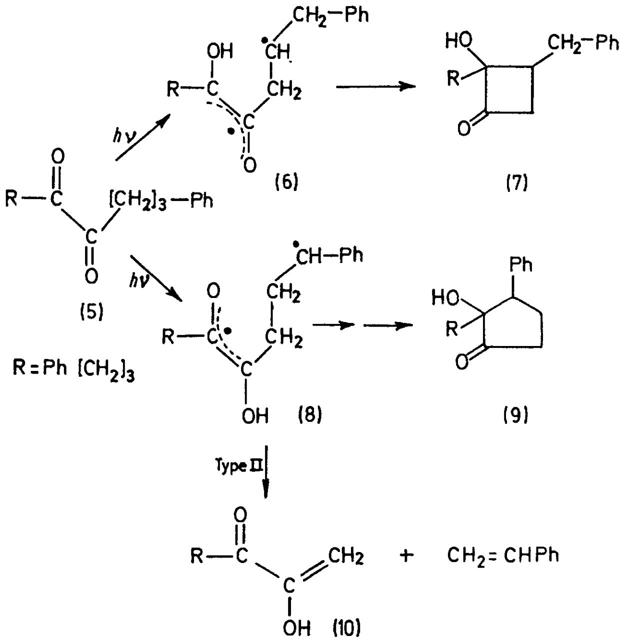
Summary 5,5-Dimethyl-6-phenylhexane-2,3-dione and 1,8-diphenyloctane-4,5-dione undergo Norrish Type II photoelimination but not McLafferty rearrangement.

PHOTOLYSIS of saturated acyclic 1,2-diketones produces 2-hydroxycyclobutanones quantitatively without concurrent formation of Norrish Type II cleavage products,[1] although certain other dicarbonyl systems are known to undergo such fragmentation.[2] Wagner[3] has commented that the major cause of this behaviour is probably the unfavourable geometry for fragmentation of the intermediate biradical, *e.g.* (**6**), where the π system comprising one of the radical sites is orthogonal to the bond to be cleaved. This concept has now been tested by generation of the biradicals (**2**) and (**8**) where such a limitation no longer applies, and confirmed by the consequent observation of the first two examples of this photoelimination in 1,2-diketone systems.



Irradiation of the hexanedione (**1**) with visible light in pentane rapidly gave a colourless solution containing products with identical (co-injection) g.l.c. retention times to those of the expected Type II products: biacetyl, formed by ketonisation of enol (**3**), and the isobutene (**4**). A sample of the latter isolated by preparative g.l.c. had identical i.r. and n.m.r. spectra to those of an authentic sample, while the n.m.r. spectrum of the crude photoproducts indicated the extent of Type II fragmentation to be *ca.* 15—20%.



Hydrogen abstraction by the innermost carbonyl of the 1,2-diketone chromophore, as in production of (**2**), has previously been observed from allylic[4] and benzylic[4,5] sites. Of these cases only the intermediate biradical (**8**) possessed the potential for Type II fragmentation on this basis, but the only reported photolysis products comprised (**7**) and (**9**) in the ratio 9:1.[5] This anomaly has been resolved by repetition of the photolysis of the octanedione (**5**) in pentane and the observation of product peaks with identical (co-injection) g.l.c. retention times to those of styrene and the hexanedione (**5**; R = Me), from ketonisation of enol (**10**). In this far less favourable case the extent of Type II cleavage is only *ca.* 1%. The effects of substituents and other factors on the product distribution of these photolyses will be discussed elsewhere.

The McLafferty rearrangement, the mass spectral analogue of the Type II process, has also not been observed for acyclic 1,2-diketones,[6] and as this could have been rationalised on the same basis, the mass spectra of (**1**) and (**5**) were examined. However no evidence of this process was available from the required metastable peaks or charged enol fragment *m/e* values, and as previously the favoured cleavage was production of acyl fragments.

I thank I.C.I. for a research fellowship.

(*Received, 4th October* 1972; *Com.* 1695.)

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