The Photochemistry of a Spirodienone

By D. H. HEY, G. H. JONES, and M. J. PERKINS*

(*Department of Chemistry, King's College, Strand, London* WC2R 2LS)

Summary Irradiation of the spirodienone (II; $R^2 = Me$) in benzene gives the isomeric dienone (V), but when iodine is present during the reaction only the methylenecyclopentenones (VII) and (VIII) can be isolated.

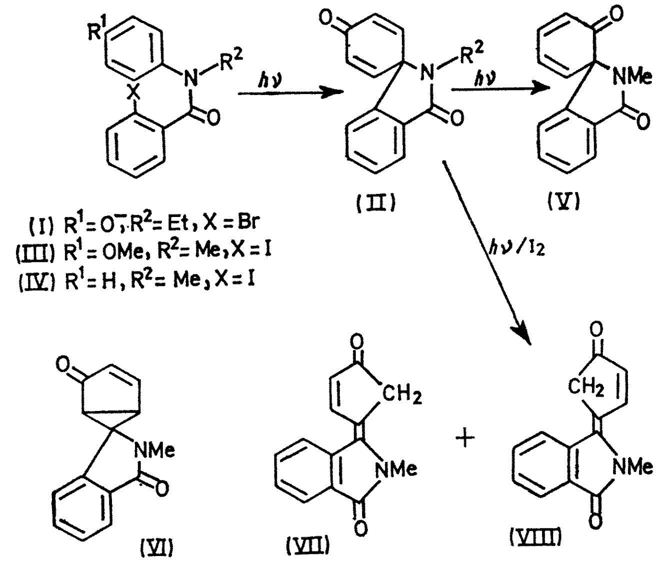
THE recent report[1] that irradiation of aqueous solutions of the phenoxide anion (I) gives the spirodienone (II; $R^2 = Et$), prompts us to report two photochemical reactions of the related dienone (II; $R^2 = Me$).

We have found that (II; $R^2 = Me$) is a product of the photolysis of (III) in oxygen-free benzene, and of (IV) in benzene saturated with oxygen.[2] The present note on the photochemistry of (II) complements both studies.

Irradiation of (II; $R^2 = Me$) in oxygen-free benzene gave a high yield of the isomeric dienone (V) as the sole identifiable product. No evidence could be found for the intermediacy of the lumiketone (VI).

The possibility that the iodine which is produced in the photolyses of (III) and (IV) might alter the course of the photo-rearrangement of (II; $R^2 = Me$), led to an experiment in which a solution of (II; $R^2 = Me$) and iodine in benzene was irradiated. Under these conditions, no (V) was produced. Instead, two new isomers of (II; $R^2 = Me$) were isolated. These were readily interconverted on irradiation, either in the presence or absence of iodine, and, on the basis of analytical and spectroscopic data, as well as hydrogenation to cyclopentanone derivatives, they were considered to be the geometrical isomers (VII) and (VIII).

Methylenecyclopentenones have been obtained from the acid-catalysed rearrangement of bicyclo[3,1,0]hexenones,[3] but our failure to detect (VI) as a product of the irradiation of (II; $R^2 = Me$) in the absence of iodine, under a variety of experimental conditions, argues against this possibility in the present reaction. The point at which the iodine diverts the reaction is therefore not yet clear.[4] Dienone (V) is not converted into (VII) and (VIII) on irradiation in benzene in the presence of iodine.



(I) $R^1 = O^-$, $R^2 = Et$, X = Br
(III) $R^1 = OMe$, $R^2 = Me$, X = I
(IV) $R^1 = H$, $R^2 = Me$, X = I

Re-examination of the products of photolysis of (III), established that (VII) and (VIII), but not (V), are formed in this reaction, and hence that iodine (or some species derived from it) is formed in sufficient quantity to control the photochemistry of the primary product (II).

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[1] Z. Horii, C. Iawata, S. Wakawa, and Y. Nakashita, *Chem. Comm.*, 1970, 1039.

[2] D. H. Hey, G. H. Jones, and M. J. Perkins, unpublished observations.

[3] H. E. Zimmerman, R. Keese, J. Nasielski, and J. S. Swenton, *J. Amer. Chem. Soc.*, 1966, **88**, 4902.

[4] A direct, uncatalysed, photorearrangement of a cross-conjugated cyclohexadienone to a methylenecyclopentenone has been noted by D. Caine, W. J. Powers, and A. M. Alejandre, *Tetrahedron Letters*, 1968, 6071.