Photocyclisation of Tri- and Tetra-phenylcyclopentenone Derivatives

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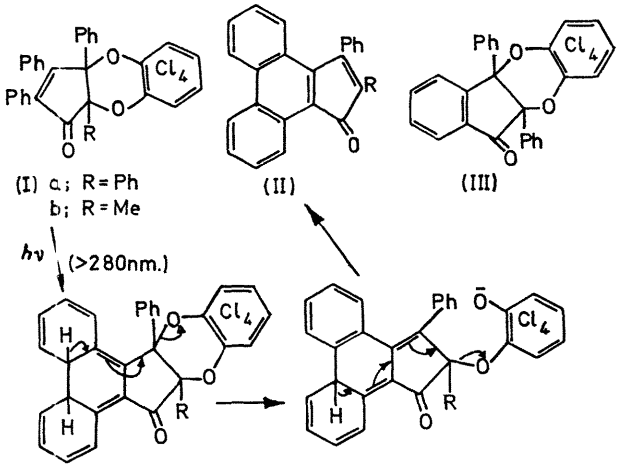
Summary The dioxen adducts obtained from the thermal reaction of *o*-chloranil and either tetracyclone or 2-methyl tricyclone have been photolysed in alcoholic solution to give cyclopentenophenanthrene derivatives.

THE oxidative cyclisation of stilbene derivatives either involving prior *trans–cis*-isomerisation of the stilbene[1] or direct cyclisation of *cis*-fused stilbenes[1,2] has been studied in detail. Recently this study has been extended to the photochemical cyclisation of tetraphenylcyclopentadienone[3] utilising the photo-excited carbonyl group as the hydrogen scavenger,[4] thus obviating the need for an external oxidant.†



I report the photochemical reaction of derivatives of tri- and tetra-phenylcyclopentenone‡ [(Ia) λ_{max} (MeOH) 309 nm. (log ϵ 4·04); (Ib) λ_{max} (MeOH) 309 nm. (log ϵ 4·06). These adducts can readily be prepared by reaction of the cyclopentadienone with *o*-chloranil in benzene solution[5] or by heating the two reactants neat at 180—190°.

Irradiation ($\lambda > 280$ nm.) of (Ia) in propan-2-ol (*ca.* 10^{-3}M) produced the cyclopentenophenanthrene (IIa) m.p. 284—286°, lit. m.p.[3] 275—276°), in 60% yield. Such a cyclisation and elimination under non-oxidative conditions raises two questions concerning a possible mechanism, *viz.* either (*a*) the cyclisation involves the phenyl groups adjacent to the *o*-chloranil utilising the quinone as the oxidant or (*b*) the phenyl groups on the enone system cyclise followed by elimination of the catechol. Irradiation of (III), however, gave 2,3-diphenylindenone and only traces of cyclised material, thus eliminating (*a*). Photolysis of (Ib) in propan-2-ol or methanol gave (IIb), m.p. 166—168°. The process was shown to be solvent-dependent, the photolysis of (Ib) in cyclohexane failing to yield identifiable products.

The large ϵ values exhibited by (Ia) and (Ib) in the u.v. spectrum show that it is impossible to differentiate between

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† Reactions of this type usually require an added oxidant, *e.g.* air or I_2.

‡ All new compounds gave satisfactory elemental analyses and/or mass spectra.

a $\pi\rightarrow\pi^*$ and an $n\rightarrow\pi^*$ transition.§ Some information can be inferred regarding the multiplicity of the excited state from photosensitisation experiments. However, in experiments using known triplet sensitisers[6] (benzophenone $E_T = 69{\cdot}1$ kcal. and acetophenone $E_T = 74{\cdot}1$ kcal.) no product could be detected spectroscopically. The choice of sensitiser was based on the knowledge that cyclopentenone has a triplet energy[7] of 61 kcal./mole and that the above sensitisers were effective in photosensitising reactions of that enone. Therefore if no sensitisation occurs in this study it is possible that a singlet is the excited state, in common with other stilbene cyclisations.[1,3] Thus cyclisation to the dihydrophenanthrene (IV) would then allow elimination of tetrachlorocatechol. The ease of such an elimination will depend on the nature of the solvent and thus, in alcohol, proton removal and solvation of the catecholate anion are possible.

The scope of the reaction with respect to leaving group and ring size is currently under investigation.

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§ Transitions with such large ϵ values are usually $\pi \rightarrow \pi^*$. N. J. Turro, "Molecular Photochemistry," Benjamin, New York, 1967; J. W. Sidman, *Chem. Rev.*, 1958, **58**, 689.

F. R. Stermitz, "Organic Photochemistry," vol. 1, ed. O. L. Chapman, Marcel Dekker, New York, 1967.

[2] R. M. Moriarty, J. M. Kliegmann, and R. B. Desai, *Chem. Comm.*, 1967, 1255; A. Schonberg and U. Sodtke, *Tetrahedron Letters*, 1967, 4977.

[3] I. Moritani, N. Toshima, S. Nakagawa, and M. Yakushiji, *Bull. Chem. Soc. Japan*, 1967, **40**, 2129; N. Toshima and I. Moritani, *Tetrahedron Letters*, 1967, 357 and 467.

[4] The use of an excited carbonyl group as a hydrogen scavenger is not novel: see ref. 1 and H. Brockmann and R. Muhlmann, *Chem. Ber.*, 1949, **82**, 348.

[5] W. M. Horspool, J. M. Tedder, and Z. U. Din, *J. Chem. Soc.* (*C*), 1969, to be published.

[6] D. R. Arnold, *Adv. Photochem.*, 1968, **6**, 328, gives a comprehensive list of ketone triplet energies.

[7] J. L. Ruhlen and P. A. Leermakers, *J. Amer. Chem. Soc.*, 1967, **89**, 4944.