

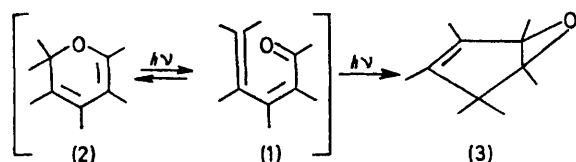
Photorearrangement of Isochromens into Indene Epoxides

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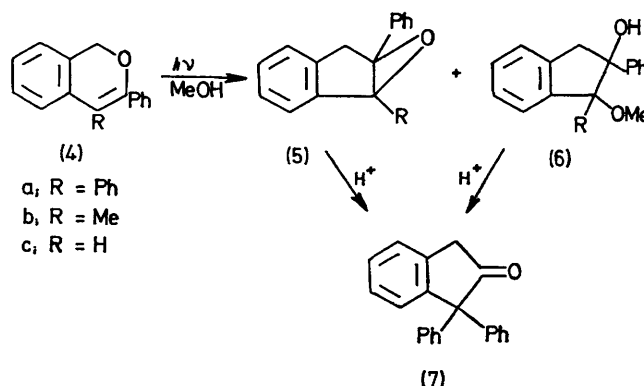
Summary Irradiation of 3,4-disubstituted isochromens in methanol give indene epoxides which produce ring-opened hydroxy-ethers on further irradiation; the mechanism involves opening of the isochromen ring to an *o*-quinonoidal intermediate which undergoes a subsequent intramolecular 4+2 cycloaddition reaction.

PHOTOCHEMICAL ring-chain tautomerization can be established between substituted *cis*-dienones (1) and 2*H*-pyrans (2),¹ and such transformations are known to be responsible for photochromism on irradiation of 2*H*-chromens² and *o*-vinyl-phenones.³ Extended irradiation of the photo-equilibrated dienone-pyran mixture might be expected to



afford an oxabicyclo[3,1,0]hex-2-ene (3) as the ultimate photoproduct by analogy with the photo-Diels-Alder reaction of hexa-1,3,5-trienes.⁴ Rearrangements of this type have been reported for nitrogen analogues,⁵ but not for oxacyclic dienes. We describe the first example of such a reaction.

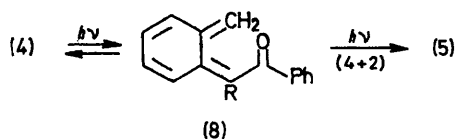
Irradiation of 3,4-diphenylisochromen† (4a), m.p. 92–93° in methanol through Pyrex using a 450 W Hanovia lamp gave two major products whose relative yields varied with the length of time of irradiation. When a 0.003M-solution



of (4a) was irradiated for 8 h, ca. 50% of starting material was consumed and the two products, isolated by preparative t.l.c., were identified as the indanes (5a), m.p. 89–90° (40%), and (6a) (10%) by comparison with authentic samples which were independently synthesized.† Irradiation for an additional 8 h gave a mixture containing mainly (6a) with traces of (5a), suggesting that (6a) is formed from a second

† All compounds gave satisfactory analyses. Complete spectroscopic and degradative details will be given elsewhere.

dary photoreaction of (5a). Treatment of (5a) or (6a) with acid resulted in their quantitative rearrangement to 1,1-diphenylindan-2-one (7).



Similar reactions were observed with the isochromens (4b, m.p. 84–85°) and (4c, m.p. 122–124°). In each case good yields of the corresponding indene epoxides were obtained after short irradiation times. At longer exposures, owing to secondary photoreactions of (5), the amount of the ring-opened product (6) increased.

The formation of the indene epoxide (5) is best rationalized by a photochemical ring opening of the isochromen ring to give a quinonoidal intermediate (8) which can either revert to starting material or undergo a subsequent intramolecular (4+2) photocycloaddition. The reactions appear

to proceed from the singlet state since the photolyses could not be sensitized or quenched with standard triplet quenchers. The low quantum efficiencies observed [*i.e.* $\Phi(4a)$ 0.02; $\Phi(4b)$ 0.002; $\Phi(4c)$ 0.004] are fully compatible with a two-photon process, in which the initially produced quinonoidal intermediate (8) partitions itself between starting material and product.

Irradiation of the closely related 2H-chromen system produces an *o*-quinoneallide intermediate which does not undergo photocycloaddition but is rather attacked by methanol to give a phenolic ether⁶. The difference in behaviour of these two systems can be attributed to the facility with which Michael addition to the labile *o*-quinoneallide intermediate occurs. This ready conjugate addition destroys the necessary chromophore for the subsequent 4+2 photocycloaddition.

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