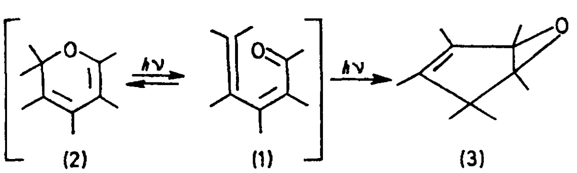
Photorearrangement of Isochromens into Indene Epoxides

By Albert Padwa,* Andrew Au, and William Owens

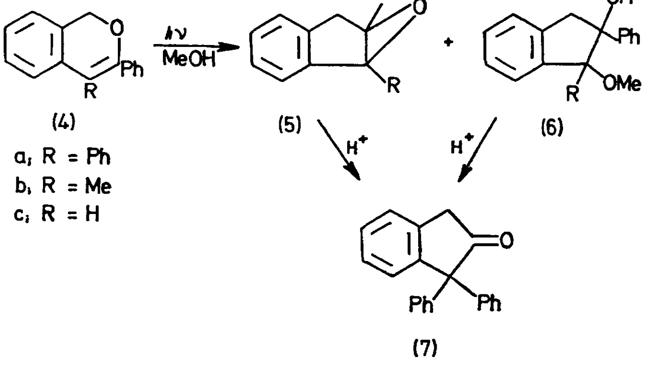
(*Department of Chemistry, State University of New York at Buffalo, Buffalo, New York* 14214)

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*-chromens[2] 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 secon-



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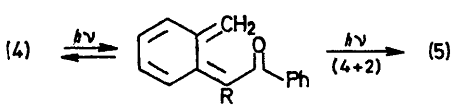
† All compounds gave satisfactory analyses. Complete spectroscopic and degradative details will be given elsewhere.

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



(**8**)

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.* Φ(**4a**) 0·02; Φ(**4b**) 0·002; Φ(**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 2*H*-chromen system produces an *o*-quinoneallide intermediate which does not undergo photocycloaddition but is rather attacked by methanol to give a phenolic ether[6] 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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