Photochemistry of Phenyloxirans;[1] Indene Oxide. A Convenient Synthesis of Isochromene

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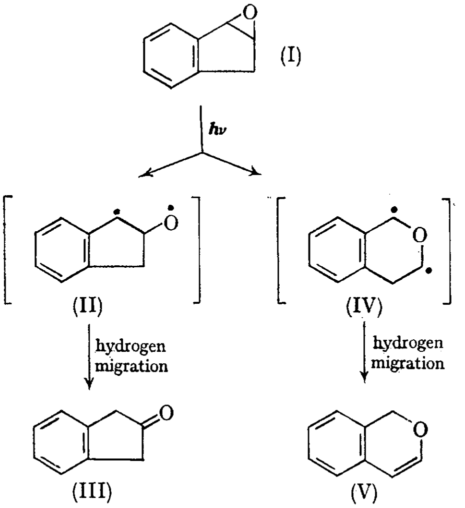
WE report a novel one-step synthesis of isochromene (V)[2] from indene oxide (I).[3] Irradiation[4] of indene oxide (I) in benzene or n-hexane affords two products, isochromene (V) and indan-2-one (III) in nearly equivalent amounts. It appears plausible that the conversion of indene oxide (I) into isochromene (V) involves initial fission of the carbon–carbon bond of the oxiran ring to give (IV). Either 1,4- or 1,2-hydrogen migration may then lead to the product, the former directly and the latter by way of a bridged *o*-xylylene. In our



opinion it is unlikely that (II) is an intermediate in the formation of (V).

The transformation of indene oxide (I) into indan-2-one (III) is analogous to the photo-rearrangement of styrene oxide and β-methylstyrene oxide to phenylacetaldehyde and phenylacetone, respectively, which were described in an earlier communication.[1b,5] Undoubtedly (III) arises through cleavage of the α-carbon–oxygen bond to form (II) followed by 1,2-hydrogen migration to oxygen or carbon. No evidence was detected for the opening of (I) to a carbene which might have been anticipated.[1] If our interpretation is correct, the rearrangement of indene oxide (I) to isochromene (V) represents the third type of behaviour to be observed upon photolysis of phenyloxirans. It is apparent from the data in the Table that the optimum yields of isochromene are obtained when the photolysis is terminated after 3 hours, since the products are photolabile and extended irradiation leads to polymer formation.

TABLE

Irradiation time*	% (I)	% (III)	% (V)**
3 hr.	37·5	32·5	30·0
7·5 hr.	28·0	42·0	30·0
24 hr.	25·0	48·0	27·0

* In benzene solution (0·19M)

** Relative amounts determined by n.m.r.

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[1] Previous papers in this series include: (a) H. Kristinsson and G. W. Griffin, *Angew. Chem. Internat. Edn.*, 1965, **4**, 868; (b) H. Kristinsson and G. W. Griffin, *J. Amer. Chem. Soc.*, 1966, **88**, 1579; (c) H. Kristinsson, *Tetrahedron Letters*, 1966, 2343.

[2] J. N. Chatterjea, *Chem. Ber.*, 1958, **91**, 2636.

[3] We are indebted to the Neville Chemical Company for a research sample of compound (I).

[4] An air-cooled Rayonet Chamber Reactor (Southern New England Ultraviolet Co., Middletown, Conn.) equipped with 16 low-pressure 8 w mercury lamps, was used as a light source.

[5] Inden-2-one (III) also may be generated thermally from indene oxide. Temperatures as low as 150° were found to be effective and precautions must be exercised to avoid rearrangement during gas–liquid–chromatographic analysis.