

PHOTOCHEMICAL REACTIONS OF 2,3-EPOXY-2-METHYL-  
3-PHENYLINDANONE

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The recent reports by Dunston and Yates<sup>1</sup> on the photochemical rearrangement of 4,5-epoxy-2,3,4,5-tetra-phenylcyclopent-2-enone and by Padwa<sup>2</sup> on the rearrangement of 4,5-epoxy-3,4-diphenylcyclopent-2-enone to isomeric 2-pyrones prompt us to report a similar transformation which we had found for an indone epoxide.

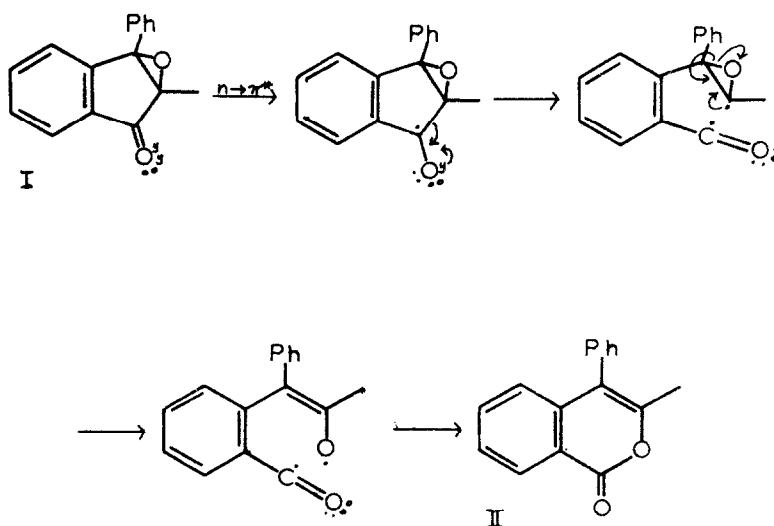
2-Methyl-3-phenylindone<sup>3</sup> was epoxidized<sup>4</sup> in alkaline methanolic hydrogen peroxide. Chromatography on silica gel to remove the by-product 3-phenylphthalide and recrystallization from methanol gave a 39.4% yield of the previously unreported 2,3-epoxy-2-methyl-3-phenylindanone (pale yellow crystals, m.p. 62.7-3.4°).<sup>\*</sup>

Photolysis of 2,3-epoxy-2-methyl-3-phenylindanone (I) for 45 min. in benzene under nitrogen (Hanovia 79A36 lamp and

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\* Satisfactory analyses were obtained for all new compounds isolated; melting points were obtained on a Fisher-Johns apparatus and are corrected.

Pyrex filter) gave 3-methyl-4-phenylisocoumarin (II)<sup>+</sup> as the principal product. One reasonable mechanism involves breaking of the carbonyl to C-2 bond,<sup>\*\*</sup> followed by that of the C-O bond next to phenyl,<sup>\*\*\*</sup> and ring closure:



<sup>+</sup> Compared with authentic material, synthesized according to DeFazi and Bertl (ref. 5).

<sup>\*\*</sup> This is a Norrish "type 1" cleavage (ref. 6), whose mechanism was discussed by us earlier (ref. 7).

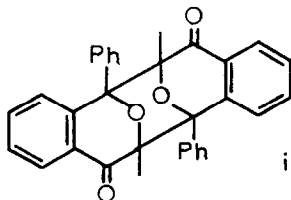
<sup>\*\*\*</sup> The "circle, dot, y" mechanistic notation (cf. ref. 7) to differentiate electrons is employed only in the excitation and acyl fission steps. An alternative mechanism has been considered by us; this has recently been discussed by Padwa (ref. 2).

Like other substituted 2,3-epoxyindanones,<sup>6</sup> this same conversion was found to occur on heating I to 95° for 5 hr. in glacial acetic acid (3.0 ml.) with a small amount (0.05 ml.) of sulfuric acid.<sup>+</sup> However, unlike the 4,5-epoxy-2,4,5-triphenylcyclopent-2-enone reported recently by Ullman,<sup>8</sup> this epoxyketone was relatively stable in hydroxylic solvents.

In the isolation of the photolysis products from 1.510 g. of I, part of II was separated from the photolysis mixture by recrystallization from ethanol, and the remaining mixture was partially separated by liquid-liquid partition chromatography.<sup>7</sup> This gave a dimer<sup>\*\*\*</sup> of I (85 mg., 5.6%; m.p. 221-222°), small amounts of two unidentified compounds, traces of anthraquinone,<sup>\*\*\*\*</sup> and a mixture of I and II from which II could be only partially separated. The total yield of II isolated was 27%.

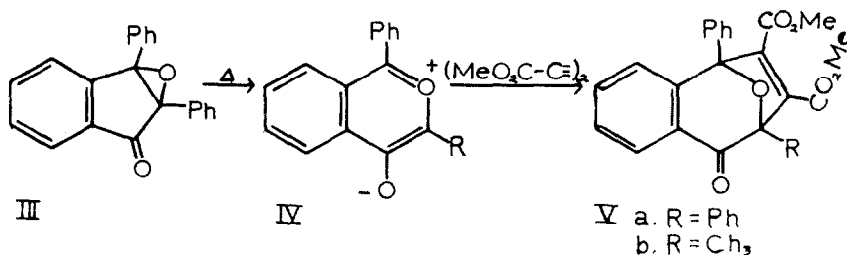
<sup>+</sup> These authors found that the reaction to give the isocoumarin proceeded considerably faster than this, perhaps because their compounds had phenyl groups at both the 2- and 3-positions.

<sup>\*\*</sup> Satisfactory analysis and M.W.; U.V. similar to I and carbonyl at 5.87  $\mu$ . The simple N.M.R. spectrum (unsplit peak at 8.61  $\tau$ ), suggests structure 1.



<sup>\*\*\*\*</sup> During earlier, unreported, photolyses of this epoxyketone in 95% ethanol, II was again the main product, along with anthraquinone, o-benzoylbenzoic acid, and several unidentified products; none of the acid was produced during the photolysis in benzene.

During the photolysis, it was noted that the solution quickly turned a bright orange, which faded to yellow when it was exposed to air afterward.\* This behavior was similar to the photochemical and thermal valence tautomerizations reported by Dunston and Yates<sup>1</sup> for 4,5-epoxy-2,3,4,5-tetraphenylcyclopent-2-enone and those<sup>9,10</sup> reported by Ullman and Milks for 2,3-epoxy-2,3-diphenylindanone (III). The latter authors found that the dipolar ion (IVa), formed on heating III at 80-100°, could be trapped with norbornadiene or dimethyl acetylenedicarboxylate.



When a mixture of I and dimethyl acetylenedicarboxylate was photolyzed in benzene, the usual orange color did not develop, and a good yield of an adduct (m.p. 185.4-186.0°) was obtained. For example, from 204 mg. of I and an excess (1.4 moles, relative to I) of dimethyl acetylenedicarboxylate,

\* Even in a closed cell, the color faded too rapidly for the absorption curve to be obtained.

a 7 min. photolysis in 160 ml. of benzene produced 27 mg. of II and 124 mg. of adduct (38% yield). Under the same conditions, 612 mg. of I produced 61 mg. of II and 433 mg. of adduct (44% yield).

Structure Vb is assigned on the basis of the following data:  $\lambda_{\text{max}}^{\text{CHCl}_3}$  5.79  $\mu$  and 7.92  $\mu$ ;  $\lambda_{\text{max}}^{\text{EtOH}}$  231 m $\mu$  (log  $\epsilon$  4.19); N.M.R. 8.22  $\tau$  (3 H's, unsplit), 6.20  $\tau$  (3 H's, unsplit), 6.25  $\tau$  (3 H's, unsplit), 2.57  $\tau$  (mult.), 1.95  $\tau$  (mult.); satisfactory analysis and M.W.; and by analogy with Ullman and Milks' thermal adduct (Va).<sup>+</sup>

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