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THE PHOTOCHEMICAL REARRANGEMENT OF
3,4-DIPHENYL-4,5-EPOXY-2-CYCLOPENTENE-1-ONE

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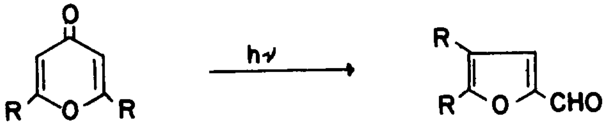
As part of a program designed to explore the photochemical behavior of a number of unsaturated epoxyketones, we have studied the photolysis of 3,4-diphenyl-4,5-epoxy-2-cyclopentene-1-one (Ib). We were led to study this particular compound in an attempt to elucidate the details of the photochemical rearrangement of 2,6-dimethyl-4-pyrone (IIa) to 4,5-dimethyl-2-furaldehyde (IIIa) (1).



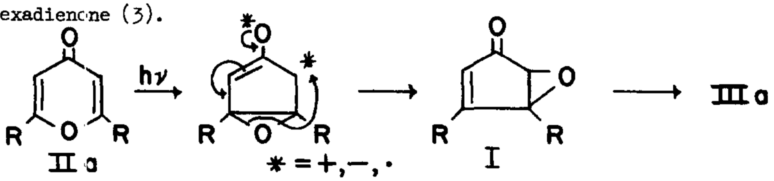
II

R = Me (IIa, IIIa)

R = Ph (IIb, IIIb)

III

Studies of the ultraviolet irradiation of 2,6-dimethyl-4-pyrone (IIa) in either the solid state or in solution have shown that a "head to tail" cage dimer was formed exclusively (2). When the photolysis was carried out under conditions chosen to retard dimerization, a low yield of an unusual rearranged product was detected (1). Yates has suggested that the mechanism of this transformation initially proceeds by a route analogous to those cases possessing the corresponding carbocyclic system, i.e. 4,4-diphenyl-2,5-cyclohexadienone (3).



The resolution of this complex photochemical transformation into a sequence of separate photochemical rearrangements necessitates a description of the intermediates involved between starting material and product. In order to confirm the role of the substituted epoxyketone as an intermediate in this sequence, 3,4-diphenyl-4,5-epoxy-2-pentene-1-one (Ib) was chosen for the present study.

Treatment of 4-hydroxy-3,4-diphenyl-2-cyclopentene-1-one (4) with 10% sodium hydroxide and 30% hydrogen peroxide in methyl alcohol readily gave rise to the epoxyalcohol. Dehydration of the tertiary alcohol with thionyl chloride-pyridine in benzene afforded in excellent yield the epoxyketone (Ib), m.p. 126-127°C; $\lambda_{max.}^{CCl_4}$ 5.84μ, 6.24μ, 11.4μ, 11.6μ; $\lambda_{max.}^{ethanol}$ 307 mμ (ε 10,300). The n.m.r. spectrum (CCl_4) of Ib shows a doublet at 6.53τ due to the methine proton and a doublet at 3.87τ due to the olefinic proton (τ =2.1 c.p.s.). The aromatic protons exhibit a multiplet at 2.78 . The peak areas are in the ratio of 1:1:10.

The initial photolysis of Ib was conducted using an internal water cooled mercury arc lamp (Hanovia, Type L-450 watts) with a corex filter to

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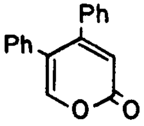
* Satisfactory carbon, hydrogen analyses were obtained for all the new compounds described herein.

eliminate wavelengths below 250mμ. A 0.2% solution of Ib in ether was purged with oxygen-free nitrogen for 45 minutes prior to irradiation and the photolysis was followed by withdrawing small samples at fixed intervals without interrupting the system. The samples were analyzed by thin layer chromatography.

We observed that the spoton a thin layer plate due to Ib had completely disappeared within 30 minutes and two new spots had appeared in its place. Further photolysis led to the reduction of one of the two new components, until after about 4 hours, only one component remained. Consideration of the product distribution obtained in a number of photolyses versus time showed an initial build up of an intermediate followed by a decrease in the amount present.

Ultraviolet irradiation of a solution of Ib in ether* for 10 minutes, utilizing a pyrex filter**, affords in almost quantitative yield a compound which has been identified as the previously discussed intermediate. This material is assigned structure IV on the basis of chemical and physical data cited below.



IV

Concentration of the solution left an oil, which rapidly crystallized on addition of hexane-benzene to give a colorless solid, IV, m.p. 118-119°C. The elemental analysis of this component (Found: C, 82.28; H, 4.98. Calcd. for $C_{17}H_{12}O_2$: C, 82.24; H, 4.87) indicates that it is an isomer of I. The infrared spectrum shows a strong carbonyl band at 5.78μ and a sharp weak spike at 6.13μ. The ultraviolet spectrum in 95% ethanol has maxima at 237mμ

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* The photolysis of methanol, benzene, carbon-tetrachloride and aqueous-dioxane solutions of Ib gave similar transformations.

** Further conversion of the initial intermediate is appreciably retarded by use of a pyrex filter.

(17,500) and 282mμ (7,100). The n.m.r. spectrum is in excellent agreement with the structure. There is a singlet at 2.60τ, a multiplet at 2.92τ, and a singlet at 3.79τ. The peak areas are in the ratio of 1:10:1. Chemical confirmation was obtained by heating IV with dimethyl acetylenedicarboxylate at 150°C for 10 hours.

The product obtained in better than 90% yield was identical to an authentic sample of 1,2-diphenyl-4,5-dicarbomethoxy benzene synthesized by the method of Alder (5).

The possibility that IV may be intermediate in the formation of a furan derivative was eliminated by the finding that the photolysis of 4,5-diphenyl-2-pyrone in ether afforded a product which has no carbonyl band in the 5.5-6.2μ region of its infrared spectrum*. This product is identical with the compound obtained by the irradiation of an ethereal solution of Ib with a corex filter. In addition, the photolysis of 2,6-diphenyl-4-pyrone (IIb) (6) gave no detectable amounts of Ib, IIIb, or IV. These data clearly indicate that Ib does not rearrange photochemically to a furan derivative**. Although the present evidence does not completely rule out the intermediacy of an epoxyketone in the rearrangement of 2,6-dimethyl-4-pyrone (IIa) to 4,5-dimethyl-2-furaldehyde (IIIa), it does appearto cast some doubt as to its presence. Experiments designed to provide further information concerning this question

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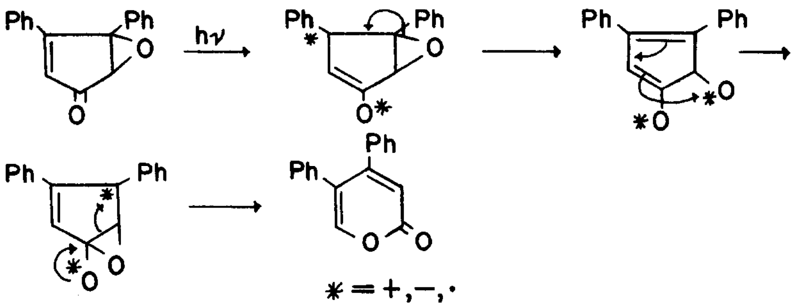
* The structure of this non-carbonyl containing compound and the photochemistry of 4,5-diphenyl-2-pyrone will be the subject of a future publication.

** Our findings appear to differ considerably from those of Ullman (7,8), who reports the existence of a photochemical valence tautomerization between 2,4,5-triphenyl-4,5-epoxy-2-pentene-1-one and the stable 2,4,6-triphenylpyrylium oxide.

are in progress.

A reasonable mechanism for the formation of IV is presented below.



It should be emphasized that the above interpretation is illustrative only, and that further work is needed to establish a structure for the excited state and the correct course of the reaction.

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