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STUDIES ON THE DECARBONYLATION AND DECARBOXYLATION REACTIONS OF 5,6-EPOXY-4,5-DIPHENYL-2-PYRONE[1]

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The current general interest in the photochemistry of both epoxides[2] and α-pyrones[3] prompts us to disclose some preliminary data concerning a number of unusual transformations of 5,6-epoxy-4,5-diphenyl-2-pyrone (I).[4,5] Our results indicate that I is remarkably versatile in its reactions and may undergo various modes of decomposition depending on the particular experimental conditions employed.

Thus treatment of I with concentrated sulfuric acid at 0° and then addition of the brown solution to water resulted in precipitation of 4-hydroxy-3,4-diphenyl-crotonic acid-γ-lactone (II) in 86% yield, m.p. 152-153°. The unsaturated lactone was identical in all respects with an authentic sample prepared by the method of Thiele.[6] Treatment of I with sodium methoxide on the other hand readily afforded methyl desylacetate (IIIA) as the major product.[7] Elucidation of the structure of IIIA was readily established on the basis of spectral evidence and comparison to authentic material independently synthesized.

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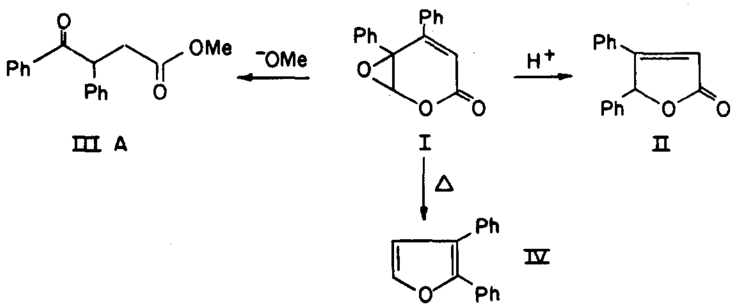
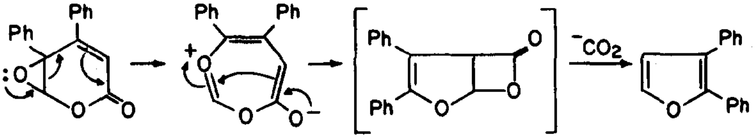


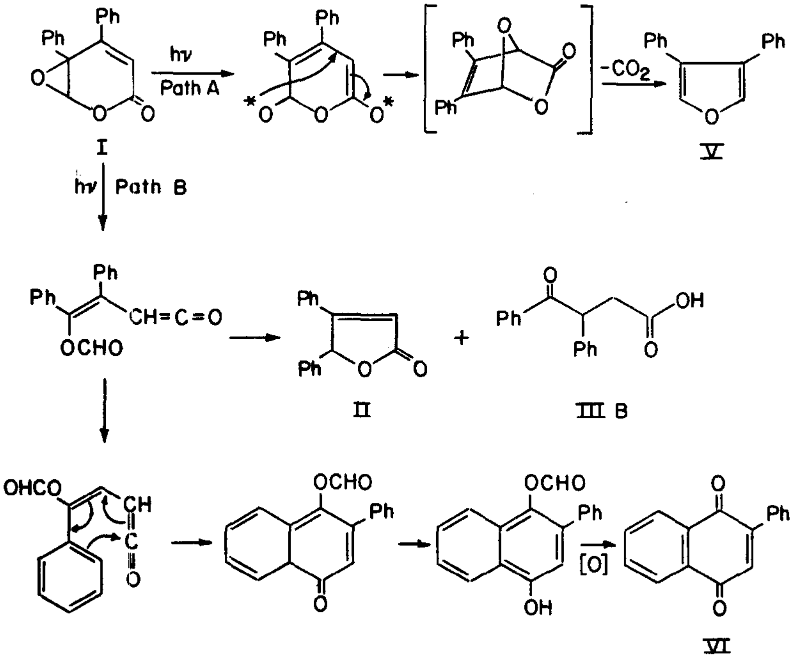
In a further study on the mode of decomposition of I, we have found that heat effects a novel decarboxylation to 2,3-diphenylfuran (IV).[8] We suggest that the reaction responsible for the formation of 2,3-diphenylfuran involves a highly reactive β-lactone which subsequently undergoes decarboxylation.



Ultraviolet irradiation of a solution of I in ether affords a mixture of four products.[9] The two major components were shown to be II (35%) and IIIB (25%). The remaining products are formed from a more complex reaction involving the formal loss of CO_2 and HCHO. These products are assigned structures V and VI on the basis of the following evidence. 3,4-Diphenylfuran (V), m.p. 109-110°, formed in 12%

yield, shows infrared absorption at 6.24, 6.50, 9.50, and 11.40, typical of a phenyl substituted furan. The ultraviolet spectrum in 95% ethanol has a maximum at 225 mμ (ε, 18,300). The n.m.r. spectrum has singlets at τ 2.48 (one proton) and τ 2.76 (five protons). Final verification was obtained by comparison with an authentic sample prepared by a procedure described by Farnum.[10] 2-Phenyl-1,4-naphthoquinone(VI), m.p. 111-112°, formed in 10% yield was characterized by the following spectral properties: Ultraviolet spectrum: λλmax (95% ethanol) 337, 303, 249 mμ (ε, 4600, 6800, 24700); infrared spectrum: λmax (KBr): 6.03, 6.30, 13.19 and 14.50 μ; 60 Mc. n.m.r. (Deuterochloroform): multiplet at τ 2.17 (nine protons), singlet at τ 2.97 (one proton). Proof of structure VI was obtained by comparison with an authentic sample.[11]

In view of these results, it appears that the observed transformations can be explained in terms of the ensuing mechanism. Path A leads to cleavage of the carbon-oxygen bond of the oxide ring followed by ring closure at the α-position.[12] Decarboxylation may then occur either thermally or photochemically from the transient lactone. The formation of VI is most easily interpreted on the basis of an initial ring fission giving the _cis_-ene-ketene followed by photoisomerization to the _trans_-ene-ketene which can cyclize in the manner described. The opening of I to a ketene by means of appropriate electron movement bears close resemblance to the reported formation of methyl β-acetonylcrotonate from the irradiation of 4,6-dimethyl-2-pyrone, a reaction which has been interpreted as a cycloelimination preceding via a ketene intermediate.[13] In agreement with this interpretation, we have found that irradiation of I in methanol afforded IIIA (60%) and V (3%). Care-



ful examination of the residue revealed no detectable amounts of VI. The isolation of ester IIIA strongly suggests the presence of a ketene intermediate which reacts with solvent to give a product different from that previously observed, but which is totally compatible with the mechanism outlined above.

Experiments designed to provide further information on the identity of the excited states and other transients responsible for these reactions are in progress.

Acknowledgment

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(4) The epoxy-pyrone I, m.p. 134-135°, was synthesized from benzil via a three-step sequence consisting of base catalyzed condensation with acetone to give 4-hydroxy-3,4-diphenyl-2-cyclopenten-1-one; epoxidation with two moles of *m*-chloroperbenzoic acid followed by dehydration of tertiary alcohol using thionyl chloride and pyridine. The structure of I was established by I.R., U.V., n.m.r. and chemical conversion to known compounds.

(5) Correct analytical data have been obtained for all new compounds reported herein.

(6) J. Thiele, *Ann.*, **306**, 196 (1894).

(7) The detailed mechanism by which I is transformed into II and III will be discussed in the full paper.

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(12) The nature of the transition involved in Path A is not defined. and consequently an asterisk is used to indicate the excited character of this state.

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