

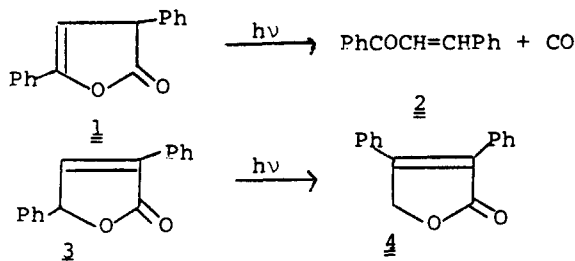
PHOTOCHEMICAL REARRANGEMENT OF 2,5-DIPHENYL-3(2H)-FURANONE

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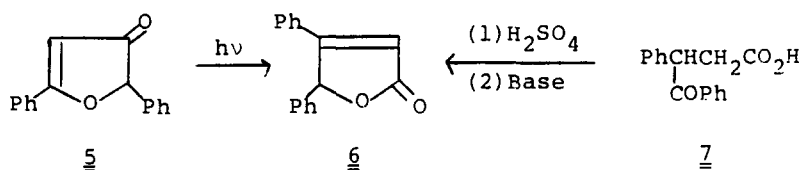
The light-induced transformations of the five-membered furanone ring system have been the subject of recent studies.¹⁻⁶ 2(3H)-Furanones (1) undergo a facile decarbonylation when subjected to ultraviolet irradiation and produce α,β -unsaturated ketones (2) as primary photoproducts.¹⁻⁵ The isomeric 2(5H)-furanone 3, on the other hand, undergoes a di- π -methane reaction from the triplet state and affords a rearranged isomer (4).⁶



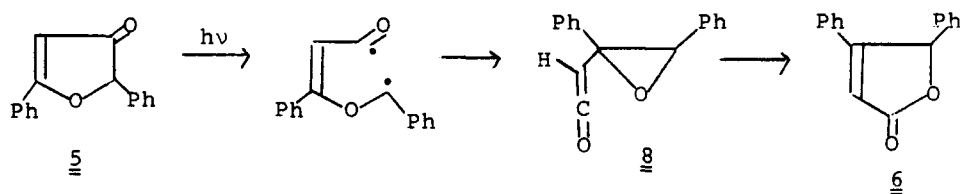
In view of the intriguing difference in photochemistry of these two systems, we decided to examine the excited state behavior of the isomeric 3(2H)-furanone 5. We now wish to report on a novel rearrangement which occurs upon irradiation of 5 and to describe some of the salient features of this reaction.

Irradiation of 2,5-diphenyl-3(2H)-furanone (5)⁷ in benzene under an argon atmosphere with Vycor-filtered light for 2.5 hr gave 4,5-diphenyl-2(5H)-furanone (6) in high yield; mp 149-150°, nmr (CDCl_3) τ 3.74 (1H, d, $J = 1.5\text{Hz}$), 3.51 (1H, d, $J = 1.5\text{Hz}$), 2.70 (m, 10H). Structure 6 was unequivocally established by an independent synthesis.⁸

An attractive pathway for the formation of 6 involves initial homolytic cleavage α to the carbonyl group to give a 1,5-diradical. Subsequent rearrangement of this species to a 1,3-diradical followed by ring closure would yield an



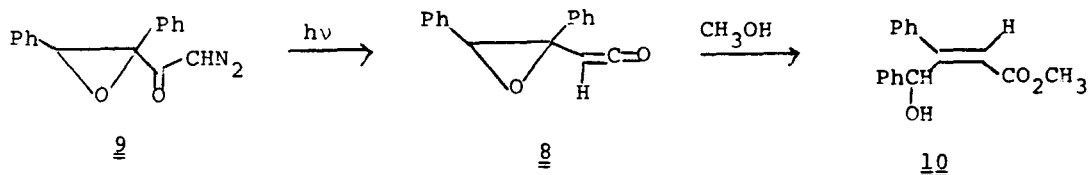
epoxy ketene (8) which is known to rearrange to the final product.⁹



The postulated transformation exemplified by 5→8 is a reverse, photochemical example of the quite general vinylcyclopropane→cyclopentene transformation.¹⁰

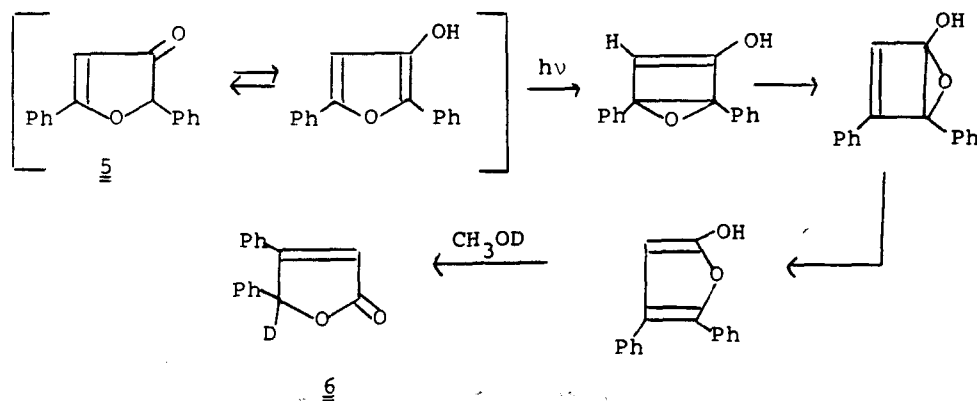
Koch has observed analogous type I cleavage reactions with related keto imino ethers¹¹ as well as with the structurally related 2-oxazolin-4-one system¹² thereby providing good analogy for the above pathway.

In order to obtain supporting evidence for the intermediacy of epoxy ketene 8, the irradiation of 5 was followed by infrared spectroscopy. I.r. spectra of aliquot portions taken during the reaction showed the progressive replacement of the original carbonyl band (1710 cm^{-1}) with the carbonyl absorption band (1760 cm^{-1}) of product. A ketene intermediate could not be detected under these conditions.¹³ The irradiation of 5 was also carried out in benzene solutions containing a ten-fold excess of methanol. Zwanenburg and coworkers had previously reported that the irradiation of α,β -diphenyl α,β -epoxy-diazomethyl ketone (9) under these conditions afforded γ -hydroxy α,β -unsaturated ester 10 in 95% yield.⁹ The formation of 10 was attributed to concomitant epoxide opening during the nucleophilic reaction of methanol with the initially generated epoxy ketene 8.



All of our attempts to detect γ -hydroxy crotonate 10 from the irradiation of 5 with varying concentrations of alcohol failed. The only product obtained was 2(5H)-furanone 6 and it was formed in essentially the same yield as that obtained in benzene.

The formation of 6 under these conditions and the failure to detect epoxy ketene 8 was surprising in view of the work of Zwanenburg and coworkers.⁹ This led us to consider an alternate mechanism for the rearrangement of 5 to 6. This mechanism, which is similar to that suggested by Beak to account for the photoisomerization of 1,4,5-trimethylimidazole to 1,3,5-trimethylpyrazole,¹⁴ would require incorporation of deuterium in the 5-position of the 2(5H)-furanone ring when deuteriomethanol is used as the solvent. The nmr spectrum of the crude



photolysate, however, clearly showed that this did not occur.

To explain the formation of 2(5H)-furanone 6, we suggest that the reaction of 5 proceeds via α -cleavage to produce epoxy ketene 8 with vibrational energy

in excess of both its own ground state and the threshold for rearrangement to 6. Normally, the assumption is made that vibrational deactivation of any relatively complex molecule is extremely rapid and that vibrationally excited states are not important in solution photochemistry.¹⁵ Nevertheless, certain photochemical reactions behave in solution very much as though vibrationally excited ground-state intermediates might be involved.¹⁵ Ullman has pointed out that the vibrational energy in a species derived by isoenergetic crossing from an electronically excited state may be concentrated in certain bonds rather than having its vibrational energy randomly distributed throughout the molecule.¹⁵ We consider this explanation as the most likely rationale to account for the details associated with the rearrangement of 3(2H)-furanone 5. It should also be noted that there is precedent in the literature for the postulation of the intermediacy of photochemically generated ketenes that undergo rearrangement faster than they react with protic solvents.¹⁶

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