Tetrahedron Letters No. 22, pp 1979 - 1982.　　0040-4039/79/0522-1979$02.00/0

# PHOTOCHEMICAL REARRANGEMENT OF 5,5-DIARYL-2,5-DIHYDROFURANS

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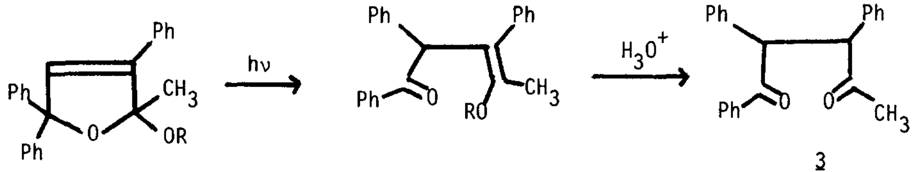
Abstract: Direct irradiation of 5,5-diaryl-2,5-dihydrofurans results in a di-π-methane rearrangement to give 3-penten-1-one derivatives. Triplet sensitization leads to the formation of a 2-oxabicyclo[2.1.0]pentane which is extremely sensitive to heat and oxygen.

The light-induced transformations of the five-membered furanone ring system have been the subject of recent studies.[1-4] 5,5-Diaryl-2(5*H*)-furanones undergo aryl group migration when subjected to ultraviolet excitation.[3] In view of the intriguing nature of this rearrangement, we thought it worthwhile to determine whether comparable photochemistry might occur with the related 2,5-dihydrofuran system. We now wish to report on a novel rearrangement which occurs upon irradiation of 5,5-diaryl-2,5-dihydrofurans and to describe some of the salient features of the reaction.

Irradiation of 2-hydroxy-2-methyl-3,5,5-triphenyl-2,5-dihydrofuran (**1**)[5] in benzene under an argon atmosphere with Vycor filtered light for 30 min gave 1,2,3-triphenyl-4-hydroxy-3-penten-1-one (**2**) in high yield. The structure of this material was unambiguously established by an acid catalyzed tautomerization to the known 1,2,3-triphenyl-1,4-pentanedione (**3**) (3:2 mixture of diastereomers).[6] Enol **2** has a relatively long lifetime (*ca* 4 hr) which is probably the result of the absence of catalytic ionic contaminants in the benzene solution. When trace amounts of an acid or base were added to the solution, enol **2** spontaneously isomerized to the more stable keto tautomer. A similar irradiation of dihydrofuran **4** gave enol ether **5** which



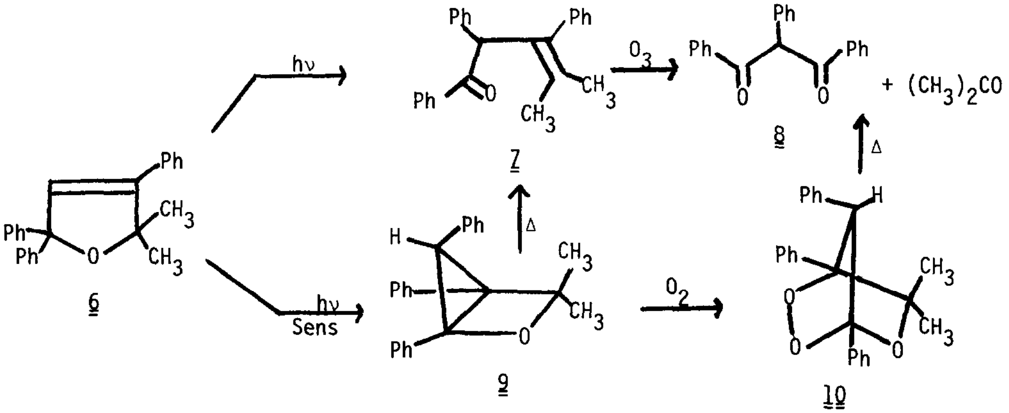
**1**; R=H
**4**; R=CH$_3$

**2**; R=H
**5**; R=CH$_3$

**3**

could readily be converted to 3 on treatment with aqueous acid.

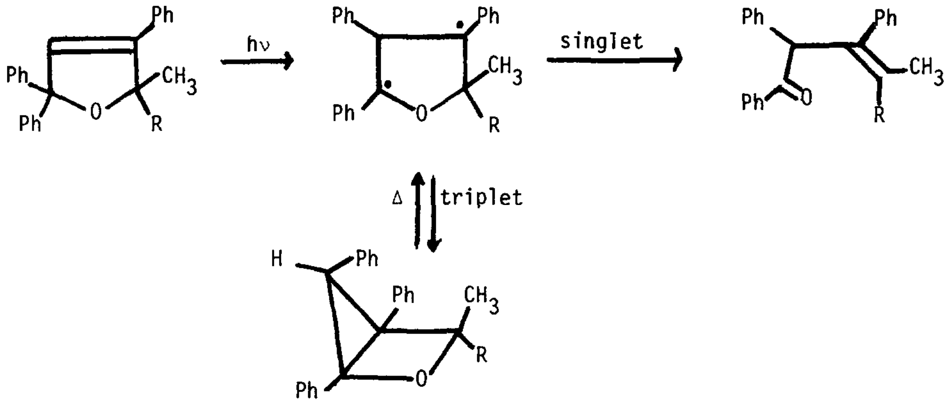
Attention was next turned to the photochemical behavior of 2,2-dimethyl-3,5,5-triphenyl-2,5-dihydrofuran (6). Irradiation of a dilute solution of this compound in benzene gave 1,2,3-triphenyl-4-methyl-3-penten-1-one (7) (76%) as a crystalline solid, mp 115-116°C. The structure of 7 was established by ozonization to acetone and 1,2,3-triphenyl-1,3-propanedione (8). Diketone 8 was verified by comparison with an authentic sample.[7] The photochemical rearrangement



encountered on the direct irradiation of dihydrofuran 6 proceeds through the singlet manifold since triplet sensitization of this compound with thioxanthone resulted in the exclusive formation of 3,3-dimethyl-1,4,5-triphenyl-2-oxabicyclo[2.1.0]pentane (9) (NMR ($CDCl_3$, 100 MHz) δ 0.92 (s, 3H), 1.40 (s, 3H), 3.08 (s, 1H) and 6.9-7.8 (m, 15 H)).[8] This material was found to be quite sensitive to heat and oxygen. Heating a degassed sample of 9 at 50° for 15 min resulted in the quantitative formation of pentenone 7. When 9 was exposed to oxygen at room temperature, it was rapidly converted to 1,4,7-triphenyl-2,5,6-trioxabicyclo[2.2.1]heptane (10) in 90% yield, mp 122-123°, NMR ($CDCl_3$, 100 MHz) δ 1.10 (s, 3H), 1.57 (s, 3H), 4.34 (s, 1H), 7.1-7.7 (m, 15H); m/e 300 ($M^+$-$(CH_3)_2CO$). Thermolysis of 10 at 120° gave acetone and propanedione 8 in high yield.

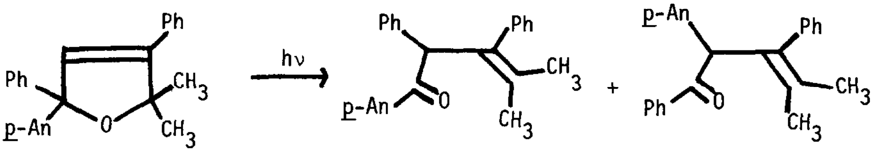
The mechanism involved in these reactions can be most readily accounted for by the pathway outlined in Scheme I. The nature of the photoproducts clearly points to a di-π-methane rearrangement as the primary photochemical step.[9] Fragmentation of the singlet 1,3-diradical yields the observed β,γ-unsaturated ketone directly. This transformation is analogous to the well studied di-π-methane rearrangement to 4,4-diphenylcyclopentenones[10,11] and 2,3,5,5-tetraphenyl-2,5-dihydrofuran.[12] The gross difference in the nature of the product obtained on

Scheme I



triplet sensitization is attributable to the fact that fragmentation of the triplet 1,3-diradical represents a high energy pathway. The suggested mechanism provides an explanation for the fact that phenyl but not methyl may undergo this rearrangement; no parallel reaction occurs with 2,2,4,4-tetramethyl-3-phenyl-2,5-dihydrofuran.

In order to gain insight into the nature of the rearranging excited state, the photolysis of 2,2-dimethyl-3,5-diphenyl-5-(*p*-anisyl)-2,5-dihydrofuran (**11**) was investigated with the view that migratory aptitudes could be used as a probe for excited state electronic make up and reactivity. Irradiation of **11** in benzene gave ketones **12** and **13** in a 3:2 ratio. The structures of **12** and **13** were established by ozonization to the corresponding diketones which were identified by comparison with independently synthesized samples. The sensitized irradiation of **11** followed by thermolysis of the crude reaction mixture also afforded **12** and **13** (ratio 1.8:1). The



**11** **12** **13**

striking feature of this rearrangement is that phenyl migrates in preference to *p*-anisyl in both the direct and sensitized reactions. The migratory aptitudes encountered here differ considerably with the results obtained in the 2(5H)-furanone system[3] where p-anisyl was found to migrate in strong preference to phenyl (ratio p-An/Ph = 16/1). It would seem that the slight preference for phenyl over p-anisyl is due to stabilization of the radical center which develops at C-5 by the nonmigrating p-anisyl group. Further studies with related aryl substituted systems are in progress and will be reported at a later date.

Acknowledgement: We are grateful to the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the National Science Foundation for financial support.

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5. Lactol **1** was prepared by the addition of one equivalent of methyl Grignard to 3,5,5-triphenyl-2(5H)-furanone. Treatment of **1** with acidic methanol gave the corresponding ether **4** in high yield. The reaction of **1** with excess methyl Grignard reagent afforded **6**.
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8. The stereochemical assignment of structure **9** is based on the chemical shift of the cyclopropyl hydrogen atom and the fact that the thermodynamically most stable isomer has the 5-phenyl group located in the endo position. Further support for the assignment will be presented in a subsequent paper.
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(**Received in** USA 14 February 1979)