

PYRYLIUM 3-OXIDE AND 4,5-EPOXY-2-CYCLOPENTENONE

VALENCE TAUTOMERISM

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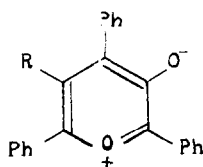
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ULLMAN<sup>1</sup> has recently described an interesting study of the photochemical valence tautomerism of 2,4,6-triphenylpyrylium 3-oxide (I). He showed that a photo-equilibrium can be established between (I) and a tautomer. The latter was not obtained in crystalline form, but spectral and degradative evidence supports its formulation as 4,5-epoxy-2,4,5-triphenyl-2-cyclopentenone (II). We report here related results in the tetraphenyl series.

The epoxide (III), m.p. 152-152.5° dec., has been prepared by two routes: (i) oxidation of tetraphenylcyclopentadienone with hydrogen peroxide in pyridine/ aqueous sodium hydroxide, and (ii) treatment of 5-chloro-4-hydroxy-2,3,4,5-tetraphenyl-2-cyclopentenone<sup>2</sup> with aqueous base. The latter reaction has previously been investigated by Pütter and Dilthey<sup>2</sup>, who assigned structure (IV) to the product; the revised structure (III) is assigned on the basis of spectroscopic data:  $\lambda_{\text{max}}^{\text{CCl}_4}$  5.79 $\mu$ ,  $\lambda_{\text{max}}^{\text{EtOH}}$  233  $\mu$  ( $\epsilon$  17,000), 338  $\mu$  ( $\epsilon$  7,100).

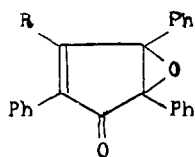
<sup>1</sup> Ullman, *J. Amer. Chem. Soc.*, 1963, 85, 3529

<sup>2</sup> Pütter and Dilthey, *J. prakt. Chem.*, 1937, 149, 183; 150, 40  
We thank Professor D.G.Farnum, Cornell University, for calling our attention to this work.



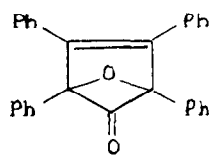
(I, R = H)

(VI, R = Ph)



(II, R = H)

(III, R = Ph)

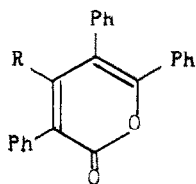


(IV)

Pütter and Dilthey<sup>2</sup> observed that (III) in acetone solution on irradiation with sunlight is converted to tetraphenyl-2-pyrone (V) with transient pink coloration of the reaction solution. We have found that irradiation of solutions of (III) in 95% ethanol or benzene in Pyrex vessels with sunlight or ultraviolet light leads to the rapid formation of a product with  $\lambda_{\max}^{\text{EtOH}}$  475 m $\mu$ ,  $\lambda_{\max}^{\text{C}_6\text{H}_6}$  510 m $\mu$ , and slower formation of the pyrone (V). The former product, which slowly reverts to III on cessation of irradiation, was shown not to be an intermediate in the formation of the latter. Its origin and the similarity of its visible spectrum to that of (I)<sup>3</sup> ( $\lambda_{\max}^{\text{EtOH}}$  494 m $\mu$ ,  $\lambda_{\max}^{\text{isooctane}}$  519, 535 m $\mu$ ), both in respect to band position and high solvent-dependence of band position, suggested that it is the pyrylium 3-oxide (VI). This was confirmed by the isolation and characterization of the crystalline perchlorate (VII), fluorescent yellow-green needles, m.p. 278-279° dec.,  $\lambda_{\max}^{\text{CH}_2\text{Cl}_2}$  2.86, 6.25, 6.37, 7.16, 7.33, 8.36, 9.10 (v.s.)  $\mu$ ,  $\lambda_{\max}^{\text{EtOH-HClO}_4}$  287, 415 m $\mu$  [cf. I in EtOH-HClO<sub>4</sub><sup>3</sup> (i.e. (VIII))]:  $\lambda_{\max}^{\text{EtOH-HClO}_4}$  285, 355, 422 m $\mu$ ]. The perchlorate dissolved in 95% ethanol to give a red solution ( $\lambda_{\max}^{\text{EtOH}}$  255, 300, 475 m $\mu$ ) indicating that reversion to (VI) occurs in this medium [cf. behaviour of (VIII)<sup>3</sup>]; irradiation of this solution

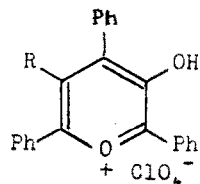
<sup>3</sup>Suld and Price, *J. Amer. Chem. Soc.*, 1962, 84, 2094.

led to rapid formation of (III) and slower conversion to (V).



(V, R = Ph)

(IX, R = H)

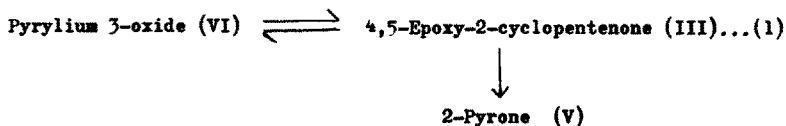


(VII, R = Ph)

(VIII, R = H)

The photochemical interconversion of (III) and (VI) is analogous to that observed by Ullman in the triphenyl series;<sup>1</sup> however, he did not observe concurrent photochemically induced rearrangement of (I) or (II) to the corresponding 2-pyrone (IX). He found that (II) is very rapidly converted to (IX) at room temperature by hydroxylic solvents. By contrast, (III) can be recrystallized unchanged from methanol<sup>2</sup> or 95% ethanol although conversion to the pyrone (V) occurs at the melting point, accompanied by formation of (VI) (red melt,  $\lambda_{\text{max}}^{\text{EtOH}}$  475 m $\mu$ ).

Thus in the tetraphenyl series, each reaction in scheme (1) can proceed by either a photochemical or thermal pathway.



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