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PHOTOLYSIS OF PYRACYLOQUINONE IN METHANOL. AN EXAMPLE OF BENZENOID-QUINOID VALENCE TAUTOMERISM

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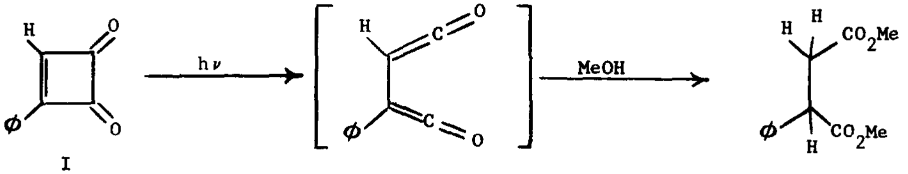
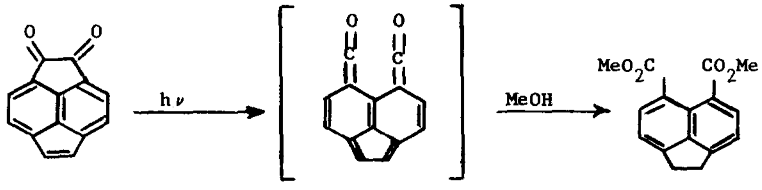
The intermediate formation of ketenes in photochemical reactions of unsaturated ketones has often been invoked and is well documented by indirect evidence.[1] Recently the direct observation by infrared spectroscopy of a ketene intermediate in a photochemical reaction was reported.[2] One particularly interesting example of this type of reaction involves irradiation of 3-phenylcyclobutene-1,2-dione (I) in methanol to yield dimethyl 2-phenylsuccinate[3] which is postulated to form via a diketene intermediate. If the photo-induced valence tautomerism of I occurs in an aromatic system such as pyracyloquinone (II)[4] the intermediate diketene thus formed would be a quinoid valence tautomer of II. We now wish to report that irradiation of a methanolic solution of II leads to formation of dimethyl 5,6-acenapthenedicarboxylate (III) in 30% yield. This is in contrast to the photolysis of 1,2-diketopyracene (IV) which gave no reaction under identical conditions. These observations represent indirect evidence for benzenoid-quinoid valence tautomerism which may be illustrated by the following simplified mechanism:



I



II

III

In a typical run, a stirred solution (2.5 x 10^{-4} M) of II in spectroquality methanol in a Pyrex flask was flushed with argon for two hours followed by irradiation (3500 Å) in a Rayonet reactor for 48 hours. The course of the reaction was monitored by the disappearance of absorption at 3080 Å. Ultraviolet spectral changes associated with the photolysis are illustrated in Figure 1. The photoproduct, a yellow-orange solid, was chromatographed over Florisil. Elution of III with chloroform was followed by its strong blue fluorescence. The elemental analysis, infrared spectrum (ν_{max} = 1720 cm^{-1}), mass fragmentation pattern (parent molecular ion, m/e 270; base peak 239) and nmr spectrum [2.25 (4H), quartet (J_{AB} = 7 cps); 6.12 (6H), singlet; 6.51 (4H) singlet] are consistent with structure III. The pure compound, mp 176-8°[5] ($\lambda_{max}^{CH_3OH}$ = 233, 314 mμ), was also identified by comparison of its physical and spectral properties with those of an authentic sample prepared from IV by peracid oxidation followed by Fischer esterification. The preparation of IV was carried out by a modified procedure[6] adapted from that of Richter and Stocker.[7]

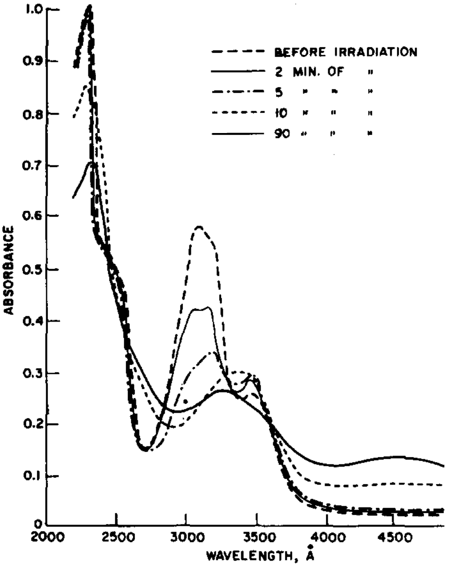
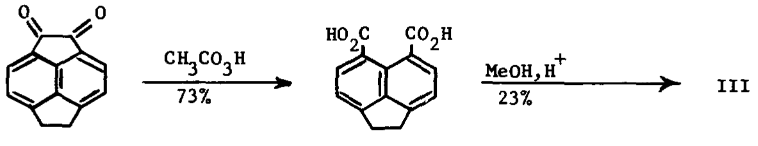


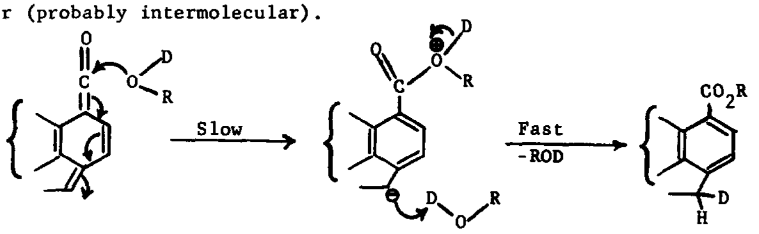
Figure 1

Changes in the ultraviolet absorption spectrum of pyracyloquinone in methanol during photolysis (3500 Å). Initial pyracyloquinone concentration 2.5 x 10^{-4}M; cell path = 1.00 mm.



IV

Ferrioxalate actinometry[8] gave $\Phi = 0.30 \pm .03$ for disappearance of II in both methanol and methanol-O-d. The mass fragmentation pattern of the diester isolated from the methanol-O-d reaction indicated that two deuterium atoms had been incorporated (parent molecular ion, m/e 272). In addition no changes in the absorption spectrum of a cyclohexane solution of II were observed even after prolonged exposure (48 hours) to 3500 Å light. The formation of the diketene (if it indeed occurs in this medium) must therefore be reversible. These preliminary results suggest a mechanism[9] which involves attack of methanol on one carbonyl group of the diketene in a slow step followed by rapid proton transfer (probably intermolecular).



The mechanism of the overall reaction, however, appears to be more complicated than that depicted above. This is illustrated by examination of changes in the visible absorption spectrum during the photolysis (Figure 2). The rate of formation of a long

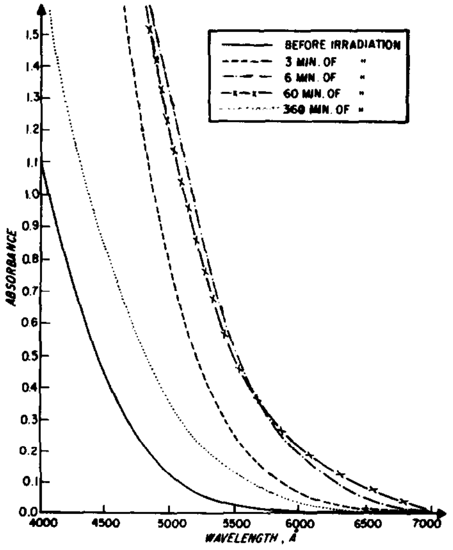


Figure 2

Visible absorption spectrum changes of pyracyloquinone in methanol during photolysis (3500 Å). Initial concentration 4.0×10^{-4}M; cell path = 5.000 cm.

wavelength (~5000 Å) absorbing species approximately corresponds to the rate of disappearance of II (compare to Figure 1). As irradiation is continued, however, this species[10] reacts further and at a rate comparable to that for formation of III.[11] Attempts to isolate and identify the intermediate(s) in this process are currently underway.

Photolysis of solutions of II in ethanol and isobutanol and with p-anisidine in benzene are characterized by spectral changes similar to those observed in the methanolic photolysis of II. Further studies on the scope and mechanism of the reaction with protic substances are in progress.

REFERENCES

1. G. Quinkert, Angew. Chem. Intern. Ed. Engl., **4**, 211 (1965) and references therein. Several recent examples have been reported by P. M. Collins, H. Hart, J. Chem. Soc., **1967**, 1197 and J. E. Baldwin, M. C. McDaniels, J. Am. Chem. Soc., **89**, 1537 (1967).
2. O. L. Chapman, J. D. Lassila, J. Am. Chem. Soc., **90**, 2449 (1968).
3. J. D. Roberts, F. B. Mallory, J. Am. Chem. Soc., **83**, 393 (1961).
4. B. M. Trost, J. Am. Chem. Soc., **88**, 853 (1966).
5. A. G. Anderson, R. G. Anderson, J. Org. Chem., **22**, 1197 (1957). These workers report a melting point of 138-141° but do not provide complete spectral data for characterization.
6. B. M. Trost, University of Wisconsin, private communication.
7. H. J. Richter, F. B. Stocker, J. Org. Chem., **24**, 366 (1959).
8. J. G. Calvert, J. N. Pitts, Photochemistry, John Wiley and Sons, New York (1966) p. 783.
9. An alternative mechanism suggested by a referee involves thermally reversible addition of methanol to one carbonyl group of II followed by photoinduced benzeneoid-quinoid valence tautomerism and subsequently thermal addition of a second methanol molecule.
10. This species is probably not the ketene ester intermediate expected from the proposed mechanism since it would react thermally with methanol to give III. This conclusion is supported by the fact that no change in the absorption spectrum of the methanolic solution of this species occurs after prolonged refluxing (24 hours).
11. This rate was determined by isolation of III from the reaction mixture at various time intervals.