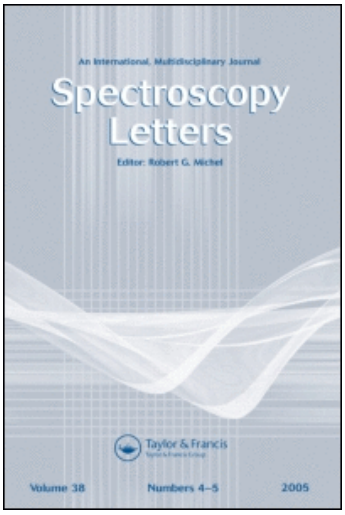

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The Mass Spectral Behavior of Hydroxyaryldiarylacetic Acid Lactones

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The Mass Spectral Behavior of Hydroxyaryldiarylacetic Acid Lactones

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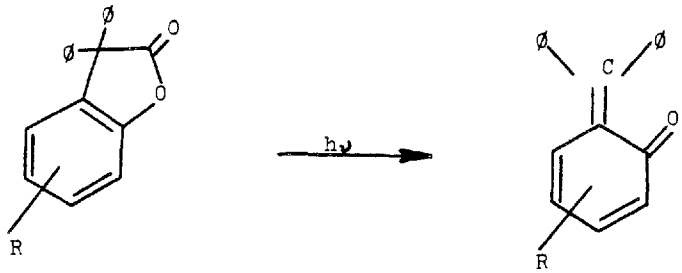
During the investigation of the photochemical decarbonylation of aryl lactones[1] as a simple synthesis of o-fuchsones of general type 2, both the starting lactones 1 and the photoproducts 2 were examined by mass spectrometry.

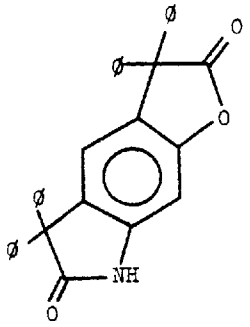


1 2

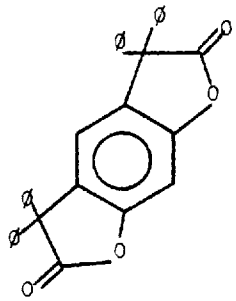
Two common features of the fragmentation pattern of all the lactones investigated (Table I) were the initial loss of CO to give a stable (M-28)

ion, followed either by loss of hydrogen to give the base (M-29) ion, or the production of an (M-105) ion as illustrated in Table II for lactone

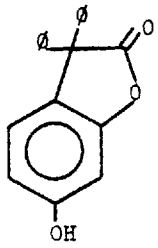
Table I



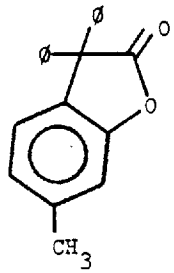
11 mp 258°



12 mp 224°



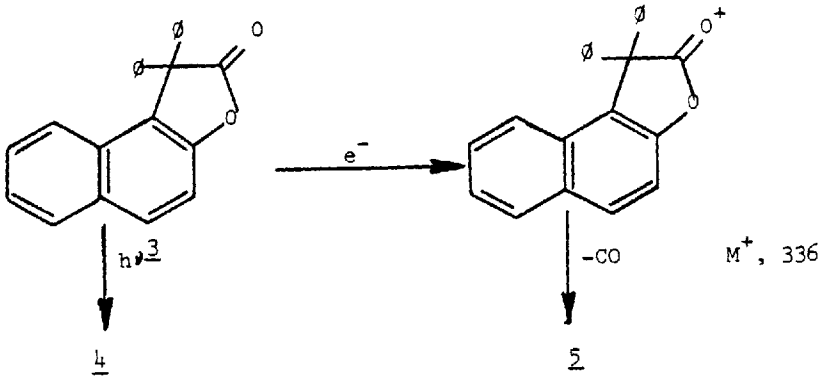
13 mp 167°



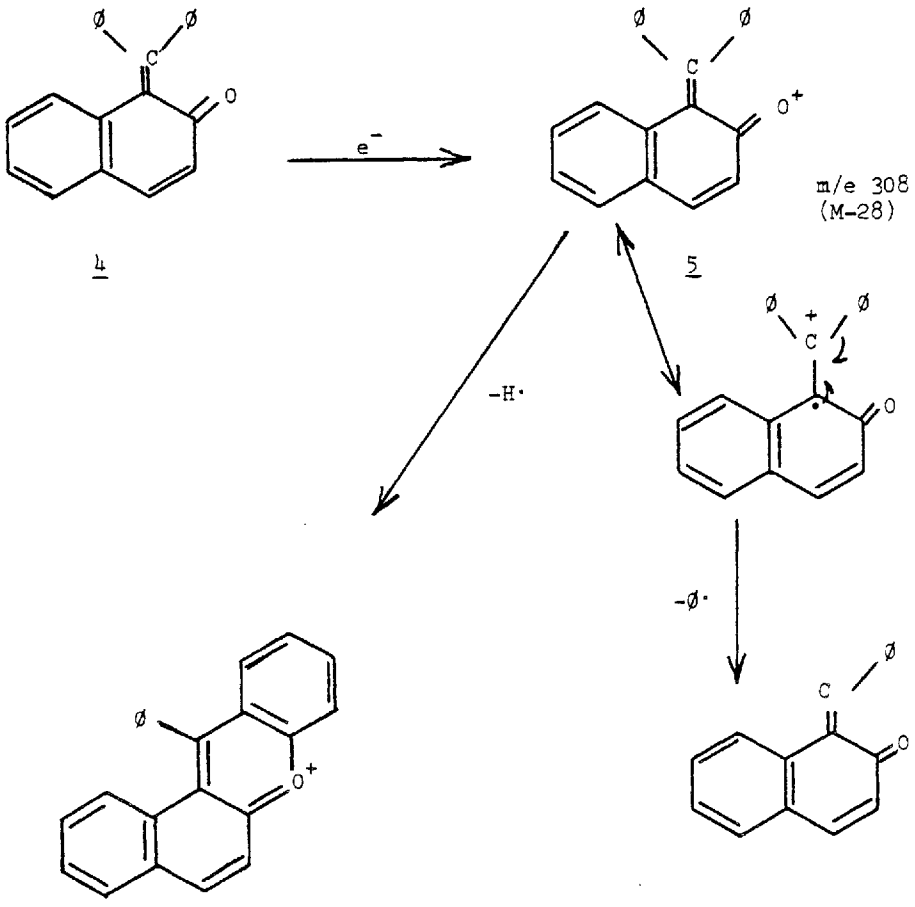
14 mp 125°

ion, followed either by loss of hydrogen to give the base (M-29) ion, or the production of an (M-105) ion as illustrated in Table II for lactone 3.

Table II



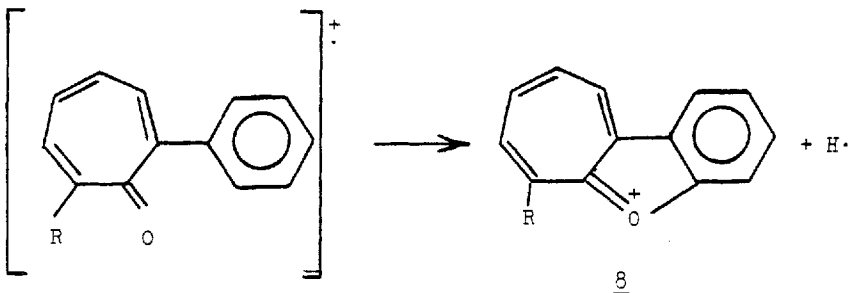
4 5



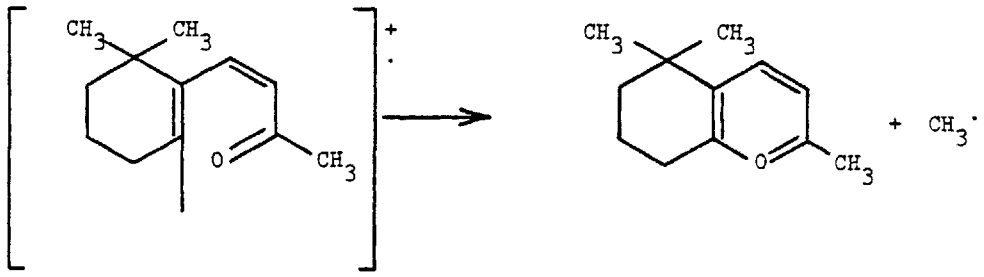
4 5

7 100%
m/e 307
(M-29)

6
m/e 231
(M-105)

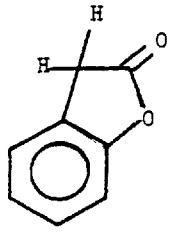


8



β-Ionone, 9

m/e 177, 100%



10

The parent ion of 3 loses CO in a manner similar to its photochemical decarbonylation. While the photochemical reaction stops at the fuchsone 4 stage, the corresponding ion 5, from the loss of CO by electron bombardment, fragments further by either loss of phenyl to give the m/e 231 ion 6 or by loss of hydrogen to give a m/e 307 ion 7.

The latter path is pictured as involving an electrophilic attack of the oxygen radical 5 on one of the phenyl rings prior to the loss of a hydrogen atom to form the stable pyrylium ion 7, similar to the pathway leading to the analogous ion 8[2], or the cyclization of -Ionone 9[4].

In support of the above fragmentation pattern, metastable ions were observed for the transition 336 to 308 (M* 282.1), 308 to 231 (M* 173.2) and 308 to 307 (M* 306.0).

The mass spectrum of the fuchsone 4, prepared from the lactone 3 by photolysis, was identical to that of 3 at mass numbers lower than (M-28) in the latter spectrum.

An indication that the loss of hydrogen from 5 occurs from one of the two phenyl groups rather than elsewhere in the molecule was inferred by examining the mass spectrum of the simpler lactone 10. In this case, the (M-28) ion fragmented further by losing a second molecule of carbon monoxide similar to the loss of this mass unit from phenols[3].

The mass spectra of the lactones 11 and 12 (Table I) contained intense peaks at (M-29) and (M-105). Pathways analogous to those suggested for lactone 3 may be envisioned for the formation of these two fragments.

Experimental

General: All melting points were taken on "uni-melt" capillary melting point apparatus and are uncorrected. Infrared spectra were recorded on a Beckman IR5A spectrophotometer. Ultraviolet spectra were recorded on a Beckman DB spectrophotometer. NMR spectra were taken on a Varian A-60 spectrometer employing approximately 50 mg of sample in 0.5 ml $CDCl_3$ solutions using 1% TMS as an internal standard. Photolysis were carried out using a long wave length photochemical quartz lamp # SCT-1 supplied by Ultra Violet Products, San Gabriel, California. The kinetics were calculated using a TR 48 Analog Computer, Electronics Associates, Long Branch, New Jersey, using a routine simulation method in which the circuit was wired for a first order equation and the simulated curves fitted to the rate data. The mass spectra were obtained on a CEC 21110 mass spectrometer.

Preparation of Lactone 3: To a cooled solution of 0.05 moles of benzili acid and 0.05 moles of β-naphthol in 100 ml acetic acid was added dropwise with stirring 30 ml conc. sulfuric acid. The reaction mixture was stirred at room temperature for 30 minutes then poured into 500 ml ice-water. The crude lactone 3 which precipitated was filtered, washed free of acid with water, an

crystallized from ethanol. A recrystallized sample melted at 183° (lit. 18[illegible]

The above general method was used for the preparation of all other lactones reported in the text. All lactones reported gave the proper analytical data and the I.R., U.V. and NMR spectra were consistent with the structures shown.

Photolysis of Lactone 3: Irradiation of a 10^{-2} M solution of lactone 3 in acetone for thirty minutes yields o-naphthofuchsone 4 in 20% yield after crystallization from acetic acid. A recrystallized sample melted at 194°, lit. mp 194°[6].

A series of photochemical kinetic runs (at constant lamp intensity) in acetone[7] was performed on lactone 3 and a rate constant, $k = 2.93 \times 10^{-3}$ min^{-1}, was obtained. The rate was followed by measuring the formation of fuchsone 4 spectrophotometrically at 400 mμ and 360 mμ, ε = 2,900 and 9,800 respectively. Prolonged irradiation revealed a diminution in both the 440 mμ and 360 mμ absorptions indicative of further photochemical reactions.

The rates of decarbonylation of a number of lactones is reported in Table III.

Table III

Lactone	Decarbonylation Rates*
1-(diphenylacetic acid)-2-naphthol lactone, 3	2.93×10^{-3} min^{-1}
1,5-di(diphenylacetic acid)-2,4-dihydroxy benzene dilacetone, 12	7.6×10^{-3} min^{-1}
1-(diphenylacetic acid)-2,5-dihydroxy benzene lactone, 13	5.92×10^{-3} min^{-1}
6-(diphenylacetic acid)-1-hydroxy-3-methyl benzene lactone, 14	very slow

*All decarbonylations were carried out in acetone[7].

References

1. A. Yogev and Y. Mazur, J. Am. Chem. Soc., 87, 15 (1965).

2. J. M. Wilson, M. Ohashi, H. Budwikiewicz, C. Djerassi, Tetrahedron, 19, 2247 (1963).

3. J. H. Beynan, G. R. Lester, and A. E. Williams, J. Phys. Chem., 63, 1861 (1959).

4. Klaus Bremann, "Mass Spectrometry: Organic Chemical Applications", McGraw-Hill, New York, NY, 1964, p. 103.

5. R. Geipert, Ber., 37, 664 (1904).

6. G. W. Clough, J. Chem. Soc., 89, 771 (1906).

7. That the decarbonylation is not sensitized by the solvent, acetone, is shown by the fact that the decarbonylation proceeds at the same rate in hexane, cyclohexane, acetic acid and diethyl ether.