Photochemical Decarbonylation of Unsaturated Lactones and Carbonates

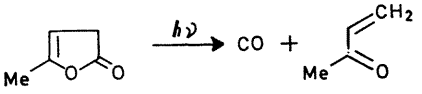
By O. L. CHAPMAN* and C. L. MCINTOSH

(*Department of Chemistry, Iowa State University, Ames, Iowa* 50010)

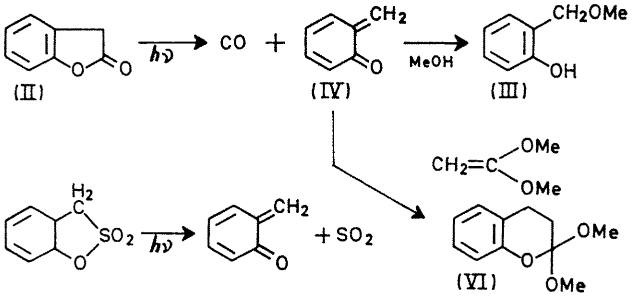
Summary Enol (and phenol) lactones readily undergo photochemical decarbonylation, and the corresponding sultones lose sulphur dioxide.

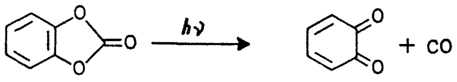
WE report a general photodecarbonylation of unsaturated lactones and carbonates which provides synthetic routes to reactive intermediates and clarifies the mechanism of certain photochemical reactions.

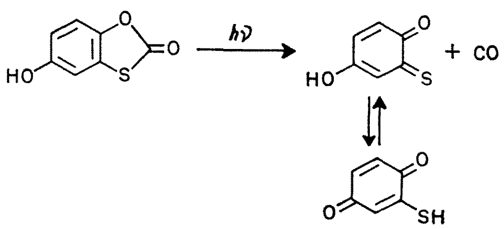
Ordinary lactones undergo various photochemical reactions giving complex mixtures.[1] However, irradiation of pent-3-en-4-olide (I) gives only methyl vinyl ketone and carbon monoxide. The reaction can be monitored by i.r. or n.m.r. spectroscopy. Irradiation of the lactone (I) at 77 K in an i.r. cell permits observations of the formation of carbon monoxide as well as of methyl vinyl ketone. The photochemical decarbonylation of the lactone (I) suggests a mechanism by which benzofuran-2(3*H*)-one (II) in methanol gives *o*-hydroxybenzyl methyl ether (III)[2] on irradiation. The photochemical step is a decarbonylation giving (at room temperature) *o*-quinonemethide which can be trapped



(I)



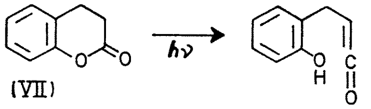




efficiently as the *ortho*-lactone (VI) (>90%) using 1,1-dimethoxyethylene. The *ortho*-lactone gives satisfactory elemental analyses and the correct parent ion (*m/e* 194) for $C_{11}H_{14}O_3$. The n.m.r. spectrum of the product shows an A_2B_2 pattern (δ 1·97 and 2·80, 4H), methoxy-protons (3·30, s, 6H), and aromatic protons (6·85, m, 4H). Hydrolysis of (VI) in dilute acid gives dihydrocoumarin. Irradiation of benzofuran-2(3*H*)-one at 77 K in a low-temperature i.r. cell[3] shows the formation of carbon monoxide and *o*-quinonemethide (ν_{max} 1656, 1565, and 1539 cm^{-1}). Light absorption by the product stops the reaction at very low conversion under these conditions.

Irradiation (room temperature) of the sultone derived from *o*-hydroxytoluene-α-sulphonic acid also gives *o*-quinonemethide. The intermediate has been trapped with 1,1-dimethoxyethylene and methanol. Irradiation in methanol gives *o*-hydroxybenzyl methyl ether and *o*-hydroxytoluene.

Photochemical reactions analogous to those of the lactone (I) and benzofuran-2(3*H*)-one can be used to generate *o*-benzoquinone derivatives from carbonates. These irradiations are carried out in solution at room temperature. *o*-Benzoquinone was identified by spectroscopic comparison with an authentic sample. The product from the monothiocarbonate was characterized by its spectroscopic properties, but not isolated. The i.r. spectrum (tetrahydrofuran; room temperature) showed bands at 1664, 1655, 1576, 1320, 975, and 785 cm^{-1}, and the n.m.r. spectrum [$(CD_3)_2SO$] showed an ABC pattern (δ_A 6·86, δ_B 6·70, and $_C$ 6·49, J_{AC} 2·8, $J_{BC}\delta$ 8·8, and J_{AB} 0·2 Hz), and a broad peak at δ 8·5 p.p.m. (OH or SH).



The decarbonylations of the unsaturated lactones, sultones, and carbonates together with the photochemical cleavage of dihydrocoumarin (VII) to a hydroxyketen[4] suggest that one critical requirement for clean photochemical cleavage of the acyl–oxygen bond in a lactone, carbonate, or ester is the presence of a double bond adjacent to the ether oxygen. Stabilization of the incipient oxyradical is apparently a determining factor in cleaving the acyl–oxygen bond.

Quinkert's studies[5] on the photodecarbonylation of 1,1,3,3-tetraphenylindan-2-one into αα'α'-tetraphenyl-*o*-xylylene provides the ketone prototype for the decarbonylation of the unsaturated lactones we have observed and for the closely related decarbonylations of *N*-phenylindol-2-(3*H*)-one reported by Fischer.[6] Fischer has provided evidence that an intermediate analogous to *o*-quinonemethide is involved in his systems.[6]

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[3] Irradiation was carried out in a low temperature i.r. cell using techniques described by O. L. Chapman and J. D. Lassila, *J. Amer. Chem. Soc.*, 1968, **90**, 2449.

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