Photo-decarbonylation of Coumarandiones

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Summary The photo-decarbonylation of coumarandiones by $n \rightarrow \pi^*$ excitation in benzene solution in the presence of certain nucleophiles produces good yields of derivatives of salicylic acid by way of a keto-keten intermediate.

RECENT interest in the solution-phase photochemistry of 1,2-diketones[1–3] and of solution phase decarbonylation reactions[4] prompts us to report our observations on the photochemistry of coumarandiones (Ia,b; and II).

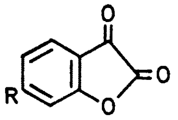
Irradiation† (λ > 280 nm, benzene solutions) of coumarandiones (Ia, λ_{max} 359 nm, ϵ 8300; Ib and II) in the presence of certain nucleophiles (water, phenols, and carboxylic acids) gives rise to derivatives of salicylic acid. The elimination of carbon monoxide (1 mole) and the concomitant decolorisation of the originally yellow solution is fairly rapid. Conventional work-up yields the products (Table). A keto-keten intermediate (IV) is suggested as the result of the decarbonylation. Although no spectroscopic evidence for the presence of the intermediate has been obtained, chemical evidence for its existence, the trapping by carboxylic acids to give mixed anhydrides (III b—d, entries 7, 8, and 9 in the Table), is compelling.

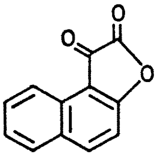
The u.v. spectrum of coumarandione (Ia) affords a little information concerning the $n \rightarrow \pi^*$ or $\pi \rightarrow \pi^*$ nature of the λ_{max} absorption. Increase in the solvent polarity brings about a small hypsochromic shift (200 cm^{-1} for a change from cyclohexane to benzene) which is characteristic of an $n \rightarrow \pi^*$ state[5] although the extinction coefficient (ϵ 8300) argues against this assignment.‡ Final proof of the involvement of an $n \rightarrow \pi^*$ state in the photo-reaction is obtained from the observed oxetan formation§ [(V), n.m.r. (CCl_4), τ 2·1—3·1 (4H, aromatic), 3·21 (1H,H_a), and 4·53 (1H,H_b), J_{AB} 5 Hz] on irradiation of coumarandione (Ia) with *cis*-1,2-dichloroethylene in benzene. The assignment that the carbonyl group α to the benzene ring is involved in oxetan formation is based on the i.r. spectrum of the oxetan (V), which exhibits a carbonyl absorption at 1810 cm^{-1} in agreement with the frequency reported[6] for the carbonyl absorption of the spiro-oxiran(VI). The choice is also influenced by earlier reports[7] of the photochemistry of alkyl benzoylformates where the α-carbonyl group undergoes photo-reduction.

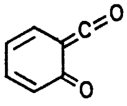
Products from the photo-reaction of coumarandiones with nuclopohiles in benzene

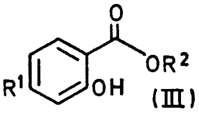
	Coumarandione	(M, in benzene)	Nucleophile	Irrad. time (hr.)	Product (%)
1.	(Ia)	(2×10^{-2})	H_2O	2·5	Salicylic acid (quant.)
2.	(Ib)	(5×10^{-2})	H_2O	2·5	*m*-Cresotinic acid (quant.)
3.	(II)	($1·8 \times 10^{-2}$)	H_2O	48	2-Hydroxy-1-naphthoic acid (94)
4.	(Ia)	($1·6 \times 10^{-2}$)	2-Naphthol	6	2-Naphthyl salicylate (24)
5.	(Ia)	($0·4 \times 10^{-2}$)	Phenol	1	Phenyl salicylate (70)
6.	(Ib)	(3×10^{-2})	Phenol	1	(IIIa) (70)
7.	(Ia)	($1·4 \times 10^{-2}$)	Benzoic acid	1	(IIIb) (quant.)[a]
8.	(Ia)	($1·4 \times 10^{-2}$)	2-Naphthoic acid	1·5	(IIIc) (quant.)[a]
9.	(Ib)	(7×10^{-2})	2-Naphthoic acid	1·5	(IIId) (quant.)[a]

[a] All new compounds gave satisfactory analytical and spectroscopic properties [(IIIb—d) and (V)].

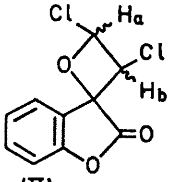

(I) a;R = H
b;R = Me

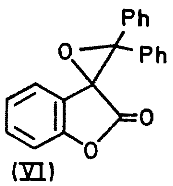

(II)


(IV)


(III)

a; R^1 = Me, R^2 = Ph
b; R^1 = H, R^2 = COPh
c; R^1 = H R^2 = CO-2-naphthyl
d; R^1 = Me, R^2 = CO-2-naphthyl


(V)


(VI)

The quantum yield (ϕ = 0·11) for decarbonylation of coumarandione is in reasonable agreement with the reported values[8] for the decarbonylation of acyl- and aroyl-formates.

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† Irradiations were carried out at room temperature in a Pyrex immersion apparatus using a 450 w medium-pressure mercury-arc lamp.

‡ A more dramatic shift is observed in the u.v. absorption when ethanol is used as solvent. This result, however, must be used with caution on account of the ready reaction between coumarandione (Ia) and alcohols to yield alkyl 2-hydroxybenzoylformates (K. Fries and W. Pfaffendorf, *Ber.*, 1912, **45**, 154, and our own observations).

§ Only carbonyl compounds which have an $n \rightarrow \pi^*$ configuration in the excited state are reactive in oxetan forming reactions. (H. Gotthardt, R. Steinmetz, and G. S. Hammond, *J. Org. Chem.*, 1968, **33**, 2774; I. W. J. Still, M. H. Kwan, and G. E. Palmer, *Canad. J. Chem.*, 1968, **46**, 373).

However, attempts to establish the electronic multiplicity of the excited state were complicated by reaction of the quenchers (piperylene and cyclohexa-1,3-diene) with the dione presumably to form oxetans.

Further studies are in progress to study the influence of photosensitisers on the reaction.

(*Received, December* 15*th*, 1969; *Com.* 1887.)

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