Photochemical Intramolecular Acylation of 3-(2-Hydroxybenzylidene)-4,5-dihydrofuran-2(3*H*)-one in Methanol

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The dependence of the kinetics on the wavelength of *trans*-3-(2-hydroxybenzylidene)-4,5-dihydrofuran-2(3*H*)-one was studied at 220—360 nm in methanol solution for the two consecutive photochemical reactions, geometrical isomerization of the *trans*- and intramolecular acylation of the *cis*-substrate. Quantum yields for the first reaction were higher (at 5.20×10^{-5}M) than those for the second. The effect of concentration quenching on quantum yields for the latter process was found to be appreciable in the 10^{-4}—10^{-5}M range. This reaction appears to proceed through long-lived T_2 states, while isomerization occurs either directly from the singlet excited state S_1 or indirectly by crossing of S_1 to a triplet excited state T_1.

THE photoinduced synthesis of coumarins from α-(2-hydroxybenzylidene)-γ-lactones was described some years ago by Zimmer *et al.*[1] A mechanistic scheme for this reaction involving the photochemical isomerization of the *trans*- into the *cis*-substrate, followed by nucleophilic attack of the phenolic hydroxy on the carbon atom of the electrophilic carbonyl group, has been

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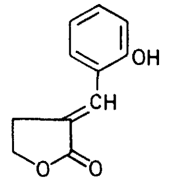
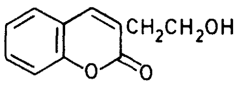
[1] H. Zimmer, F. Haupter, S. P. Kharidia, H. Pauling, R. G. Gailey, T. Pampalone, T. C. Purcell, and R. Walter, *Tetrahedron Letters*, 1968, 5435.

suggested,[1] but no evidence of any intermediate was reported, nor the relevance of the possible photochemical conversion of the *cis*-substrate into the coumarin was investigated. Our interest in the acid-catalysed intramolecular acylation of 3-(2-hydroxybenzylidene)-4,5-dihydrofuran-2(3*H*)-one (I), and the usefulness of such a molecule as a model to study the widely occurring compounds which have a carbonyl group and a double bond capable of twisting in an excited state, and which have been recently reported[2] to undergo photochemical reactions through abnormally long-lived upper excited states, prompted us to study in some detail the kinetics of the photochemical reaction, in order to measure the quantum yields as a function of wavelength, detect intermediates, and clarify their role.



(I)



(II)

EXPERIMENTAL

Materials.—*trans*-3-(2-Hydroxybenzylidene)-4,5-dihydrofuran-2(3*H*)-one *trans*-(I) was synthesized and purified as described previously.[3] Spectrograde methanol was dehydrated by refluxing and distillation in the presence of magnesium methoxide.

Irradiations.—Quantum yield studies were carried out with a 700 W high pressure mercury arc lamp (model TQ 718; Quarzlampen) which was placed in the housing of a spectrophotometer assembly mounted on optical bench and using a grating monochromator (model 33-86-25; Bausch and Lomb). By means of quartz condensing lenses the irradiating beam was focused into the spectrophotometric cell.

Potassium ferrioxalate was used for actinometry, according to the method of Hatchard and Parker.[4] Energies as a function of wavelength were measured with a passing band of 6 nm, which was also used for quantum yield measurements: in these conditions energy values range from 2.34 to 31.8 × 10^{16} quanta l^{-1} s^{-1} at 220 and 366 nm respectively.

A $(5.20 \pm 0.05) \times 10^{-5}$M solution of *trans*-(I) in anhydrous methanol was employed for irradiations. Analysis of reagent, intermediate, and photoproduct was carried out spectrophotometrically. No particular care was devoted to excluding oxygen during irradiations. No oxygen effect, in any way, could be detected in the photochemical processes studied.

Quantum yields were corrected for unabsorbed light.

Photoproducts of trans-(I).—The geometrical isomer of *trans*-(I), which was detected as a photochemical intermediate, was prepared by irradiation in 10% v/v H_2O–MeOH, a solvent in which the photochemical conversion of *cis*-(I) into the photoproduct 3-(2-hydroxyethyl)coumarin (II) was inhibited, and in which *cis*-(I) was consequently photochemically fairly stable, at least for the radiation doses employed. Compound *trans*-(I) (100 mg) in this solvent (100 ml) was irradiated until complete conversion, as checked by t.l.c. and u.v. spectroscopy. Evaporation of the solvent in the cold under vacuum yielded practically pure *cis*-(I), which was crystallized from MeOH (Found: C, 69.35; H, 5.3. Calc. for $C_{11}H_{10}O_3$: C, 69.45; H, 5.3%), $\lambda_{max.}$ (MeOH) 329 and 280 nm (ε 8 500 and 12 300 l mol^{-1} cm^{-1}). T.l.c. on GF 254 (Merck) silica gel with elution by ethyl acetate–benzene–n-hexane 100 : 100 : 60 (v/v) could easily differentiate the *cis*- (R_F 0.54) from the *trans*-isomer (R_F 0.44).

Compound *cis*-(I) was subject to thermal isomerization at temperatures about or above 120°, at which it transformed more or less rapidly into *trans*-(I). The photoisomer had carbonyl and olefinic i.r. absorptions almost identical with those of *trans*-(I). The n.m.r. spectrum (CF_3COCF_3,$0.5D_2O$) was also similar, the only noticeable differences being the deshielding effect of the carbonyl group on the vinyl hydrogen signal of *trans*-(I) at δ 7.75 (*J* 3 Hz) relative to that of *cis*-(I) at δ 7.25 (*J* 2 Hz), and the splitting of aromatic hydrogen signals of *cis*-(I) at δ 7.50 (1 H, *o*-H) and 6.85 (3 H, aromatic) compared to the unresolved signals of *trans*-(I) at δ 6.7—7.2. The deshielding of the vinyl hydrogen and the behaviour of the aromatic hydrogens in the n.m.r. spectra, as well as the relative thermal stabilities of the two isomers support the assigned geometries.

When irradiation of *trans*-(I) was carried out in anhydrous methanol the photochemical conversion of *cis*-(I) into 3-(2-hydroxyethyl)coumarin (II) proceeded, though with a lower quantum yield at 220—360 nm than that for isomerization. The ' final ' photoproduct was recovered in practically quantitative yield and identified by comparison with authentic 3-(2-hydroxyethyl)coumarin.[3]

Dipole Moment of cis-(I).—The dipole moment μ of *cis*-(I) was determined in anhydrous dioxan solution at 25.0 ± 0.05°, by the procedure described for the *trans*-isomer.[3] From the difference ΔD between the dielectric constants of solutions containing w_2 weight fractions of *cis*-(I) and the solvent ($d\Delta D/dw_2 = 6.364$), μ was evaluated as 3.15 ± 0.09 D. This value gives further support to the assigned geometry.

RESULTS AND DISCUSSION

The photochemical kinetics of *trans*-3-(2-hydroxybenzylidene)-4,5-dihydrofuran-2(3*H*)-one [*trans*-(I)] in methanol solution was found to be strongly wavelength dependent. Irradiation of *trans*-(I) produced geometrical isomerization in high quantum yield, but then, though with generally lower quantum yield, *cis*-(I), produced in the primary photochemical process, underwent a photochemical intramolecular acylation to give quantitatively 3-(2-hydroxyethyl)coumarin (II). The coumarin (II) was not photochemically stable, but, with the energy output used, at the various wavelengths the photodecomposition of (II) was a very slow process, so that no interference with the photochemical intramolecular acylation reaction resulted. In unsaturated lactone photochemistry, hydrogen abstraction from solvent was found to be strongly inhibited by traces of

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[2] E. F. Ullman and N. Baumann, *J. Amer. Chem. Soc.*, 1970, **92**, 5892.

[3] I. R. Bellobono, B. Marcandalli, L. Zanderighi, and C. Parini, preceding paper.

[4] C. G. Hatchard and C. A. Parker, *Proc. Roy. Soc.*, 1956, **A235**, 518.

oxygen.[2] Irradiations were carried out in our study without air exclusion. The complication due to hydrogen abstraction, which leads to radical reactions and mixtures of photoproducts, was thus avoided. The presence of oxygen, on the contrary, did not affect the photochemistry of isomerization and intramolecular acylation.

The different quantum yields for the two consecutive, kinetically zero order photochemical processes which have been examined [isomerization of *trans*-(I) and intramolecular acylation of *cis*-(I)], offered the possibility of following them both by spectrophotometric analysis of the reaction mixture. The spectral changes in going from *trans*- to *cis*-(I) were small (mainly differences in molar absorptivities), but, by operating at the appropriate absorbance range reproducible and reliable data could be obtained. Quantum yields, at the various wavelengths tested, for the two photochemical processes studied are reported in Table 1, with errors quoted as standard deviations.

TABLE 1

Quantum yields of geometrical isomerization [ϕ_1, reaction (1)] of *trans*-3-(2-hydroxybenzylidene)-4,5-dihydrofuran-2(3*H*)-one and of intramolecular acylation [ϕ_2, reaction (2)] of the photoisomer in 5.20×10^{-5}M methanol solution at 25°, as a function of wavelength

Wavelength (nm)	ϕ_1	ϕ_2
	(molecules quantum^{-1})	
220	1.05 ± 0.084	0.274 ± 0.023
235	0.99 ± 0.081	0.195 ± 0.018
250	0.934 ± 0.042	0.102 ± 0.010
254	0.885 ± 0.046	0.0862 ± 0.011
265	0.792 ± 0.035	0.0675 ± 0.008
280	0.674 ± 0.048	0.0498 ± 0.012
290	0.585 ± 0.061	0.0456 ± 0.009
305	0.513 ± 0.049	0.0520 ± 0.009
330	0.451 ± 0.037	0.0847 ± 0.019
360	0.410 ± 0.052	0.135 ± 0.014

As for the photochemical isomerization of 3-(benzylidene)-4,5-dihydrofuran-2(3*H*)-one,[2] the primary process must proceed either directly from the singlet excited state S_1 or indirectly by crossing of S_1 to a triplet excited state T_1 [reaction (1)]. The relative quantum

$$S_1 \longrightarrow (T_1) \longrightarrow \text{isomerization } (\phi_1) \qquad (1)$$

yields ϕ_1 were not affected by concentration quenching other than by singlet quenching at high concentrations of *trans*-(I).

On the contrary, a more pronounced effect of concentration of *cis*-(I) on the quantum yields ϕ_2 of intramolecular acylation was found, similar to that observed for the case of hydrogen reaction of the parent compound in isopropyl alcohol.[2] Experimental data for reaction (2) fitted satisfactorily well the Stern–Volmer

$$S_2 \longrightarrow T_2 \longrightarrow \text{intramolecular acylation } (\phi_2) \qquad (2)$$

equation (3)[5] where $(\phi_2)_0$ is the quantum yield extrapolated at zero concentration, τ is the lifetime of the

$$\phi_2^{-1} = (\phi_2)_0^{-1}[1 + k_q \tau C_{\text{cis-(I)}}] \qquad (3)$$

quenched excited state, k_q is the quenching rate constant, which was assumed to be equal to the diffusion controlled rate constant in methanol (1.1×10^{10} l mol^{-1} s^{-1}),[6] and $C_{\text{cis-(I)}}$ is the molar concentration of *cis*-(I).

The $(\phi_2)_0$ and τ values in Table 2 were obtained by the least squares treatment. The analogy with hydrogen abstraction,[2] especially if the difference of solvent is accounted for, does not seem to be fortuitous, with regard to the consideration that photochemical intramolecular acylation of *cis*-(I) is primarily an internal hydrogen abstraction from hydroxy to carbonyl group (internal oxidation–reduction). Intramolecular acylation thus appears to proceed through an upper excited state T_2, which probably has $^3(n,\pi^*)$ symmetry and a planar arrangement of atoms about the carbon–carbon double bond, while the triplet giving rise to isomerization is T_1, to which a $^3(\pi,\pi^*)$ state may probably be assigned, relaxing to preferred perpendicular carbon–carbon double bond geometry. This justifies the unusual concentration quenching and the moderately long lifetime of the reactive triplet.

TABLE 2

	$(\phi_2)_0$	$10^6\tau$ (s)
At 220 nm	0.98 ± 0.12	4.5 ± 0.6
At 254 nm	0.32 ± 0.04	4.7 ± 0.4
At 360 nm	0.53 ± 0.05	5.1 ± 0.3

The implication that the internal conversions $T_2\ ^3(n,\pi^*) \longrightarrow T_1\ ^3(\pi,\pi^*)$ and $S_2\ ^1(n,\pi^*) \longrightarrow S_1\ ^1(\pi,\pi^*)$ are apparently inefficient is perfectly in line with the experimental possibility of converting photochemically, with high efficiency, the *trans*- into the *cis*-isomer by equation (1), while photochemical intramolecular acylation is a consecutive reaction of *cis*-(I) following equation (2). Moreover, the above considerations are consistent with the marked influence of wavelength on quantum yields, which suggests barriers to internal conversions.

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[5] O. Stern and M. Volmer, *Z. Phys.*, 1919, **20**, 183.

[6] J. G. Calvert and J. N. Pitts, jun., 'Photochemistry,' Wiley, New York, 1966, p. 627.