Reactions of Carbonyl Compounds in Basic Solutions. Part 17.[1] The Alkaline Hydrolysis of Substituted (*E*)-5,5′-Diphenylbifuranylidenediones and 3,7-Diphenylpyrano[4,3-*c*]pyran-1,5-diones

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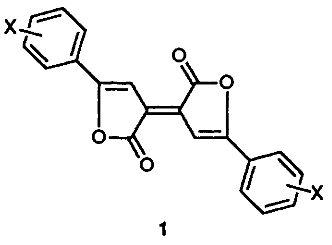
The alkaline hydrolyses of a series of substituted (*E*)-5,5′-diphenylbifuranylidenediones and 3,7-diphenylpyrano[4,3-*c*]pyran-1,5-diones have been shown to proceed by biphasic pathways. In both cases, a very rapid primary reaction gives hydrolysis of one lactone ring. This is followed by a less rapid secondary reaction giving hydrolysis of the second ring and identical products from both systems. Rate coefficients for the secondary reactions have been measured in 70% (v/v) dioxane–water at 30.0 °C and, for the parent substrates, at 49.0 °C. The enthalpies and entropies of activation have been evaluated. The effects of substitution have been assessed by means of the Hammett equation. Reaction pathways are suggested and the reactivity is related to the ring size.

In 1882 von Pechmann[2] reported an attempt to prepare 1,4-naphthoquinone from 3-benzoylacrylic acid by dehydration. However, the reaction gave a red pigment with the same empirical formula as the expected product. After several investigations over a considerable period,[3,4] these pigments, called 'Pechmann dyes', were suggested to be bridged five-membered lactones with *E*-configurations (**1**), the (*E*)-5,5′-diphenylbifuranylidenediones. The latter compounds are conveniently prepared by the treatment of 3-benzoylacrylic acid with acetic anhydride in the presence of Cu^{I} catalyst[4] and a pathway has been outlined by Begley *et al.*[5] The latter confirmed the structure of the dimesityl compound of **1** by X-ray studies.[5] The diaryl compounds of **1** have been found to rearrange into yellow or orange pigments, identified as 3,7-diphenylpyrano[4,3-*c*]pyran-1,5-diones (**2**), by heating in a solvent such as nitrobenzene and ethane-1,2-diol.[6]



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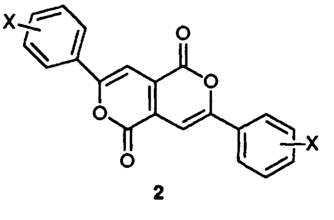

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The present investigation details a study of the alkaline hydrolysis of substituted (*E*)-5,5′-diphenylbifuranylidenediones and 3,7-diphenylpyrano[4,3-*c*]pyran-1,5-diones. The kinetics, effects of substitution and activation parameters have all been considered in formulating detailed mechanistic pathways.

Experimental

Materials.—The method used for the synthesis of the substituted (*E*)-5,5′-diphenylbifuranylidenediones was a modification of that of Fang and Bergmann.[4] The substituted (*E*)-3-benzoylacrylic acids, prepared as described previously,[7] were treated with acetic anhydride in the presence of Cu^{I} and ammonium chlorides. The diphenylbifuranylidenediones were rearranged into diphenylpyranopyrandiones by heating in a mixture of nitrobenzene and ethane-1,2-diol or propane-1,3-diol.[6] The compounds had either m.p.s in good agreement with literature values[2,4,6] or are reported in Table 1. Solvents and other materials were purified by standard procedures where required, as described previously.[8]

Kinetic Measurements.—Rate coefficients for the alkaline hydrolysis of the substrates were determined spectrophotometrically by use of Unicam SP8000 and SP8-100 spectrophotometers. The cell temperature was controlled to within ±0.05 °C by means of a Churchill thermocirculator. The reactions were followed at suitable wavelengths. These were normally those having the greatest difference between the substrate and product, and the λ_{max} values for the substrates are shown in Table 2. The procedure then followed was that described previously.[9] The substrates were dissolved in dioxane and studied at 0.5–2 × 10^{-4} mol dm^{-3}. The reaction solvent was 70% (v/v) aqueous dioxane and the base, sodium hydroxide, was studied at 1–8 × 10^{-4} mol dm^{-3}.

Product Analysis.—The products of the alkaline hydrolysis of the substrates studied here are the anions of the diphenacylfumaric acids, *cf.* reference 3. Thus the products of the alkaline hydrolysis of the parent (*E*)-5,5′-diphenylbifuranylidenedione and 3,7-diphenylpyrano[4,3-*c*]pyran-1,5-dione had almost identical UV spectra and gave, on acidification with concentrated hydrochloric acid, the more thermodynamically stable pyranopyrandione.

Structure of Diones.—The structure of (*E*)-5,5′-diphenylbifuranylidene-2,2′-dione has been confirmed by a single crystal X-ray analysis.[10] The structure is as shown (**1**, X = H) with the two five-membered lactone rings being coplanar. The angle between the planes of the phenyl groups and the lactones is 1.7°. This is in contrast to that of the sterically hindered dimesityl compound,[5] in which the 5,5′-diaryl groups are significantly twisted out of plane. The structure of 3,7-diphenylpyrano-[4,3-*c*]pyran-1,5-dione does not appear to have been confirmed in this way. However, the planar structure of coumarin[11] would indicate a similar structure to be very likely for the

Table 1 Previously unreported substituted 3,7-diphenylpyrano[4,3-*c*]pyran-1,5-diones (**2**)

		Found (%)				Required (%)			
Substituent	M.p./°C	C	H	Other	Formula	C	H	Other	Appearance
p-Br	308–310 (decomp.)	50.4	1.9	31.7 (Br)	$C_{20}H_{10}Br_2O_4$	50.7	2.1	33.7 (Br)	orange-yellow with strong fluorescence
m-NO_2	> 320 (decomp.)	59.3	2.5	6.7 (N)	$C_{20}H_{10}N_4O_8$	59.1	2.5	6.9 (N)	dark yellow-green

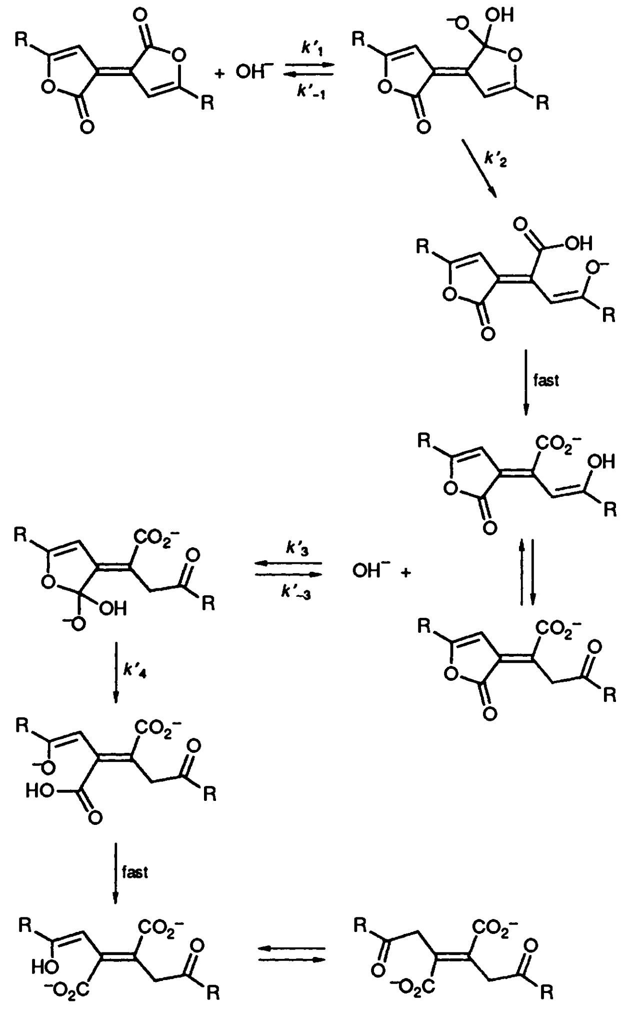
Table 2 The UV–VIS spectra of the (*E*)-5,5′-diphenylbifuranylidenediones (**1**) and 3,7-diphenylpyrano[4,3-*c*]pyran-1,5-diones (**2**) in toluene

	λ_{max}	
Substituent	**1**	**2**
H	550, 511	434
p-OMe	588, 545	454
p-Me	558, 518	440
p-Cl	558, 520	439
p-Br	560, 523	439
m-NO_2	538, 507	478

Table 3 Rate coefficients (k_2) for the alkaline hydrolysis of (*E*)-5,5′-diphenylbifuranylidenediones (**1**) and 3,7-diphenylpyrano[4,3-*c*]-pyran-1,5-diones (**2**) in 70% (v/v) aqueous dioxane at 30.0 °C[a]

	k_2/dm^3 mol^{-1} s^{-1}	
Substituent	**1**	**2**
H	639 (1100)[b]	120 (240)[b]
p-OMe	159	44.1
p-Me	167	47.6
p-Cl	1 100	340
p-Br	1 210	306
m-NO_2	10 800	230

[a] Rate coefficients were reproducible to ± 5%. [b] At 49.0 °C.



Scheme 1

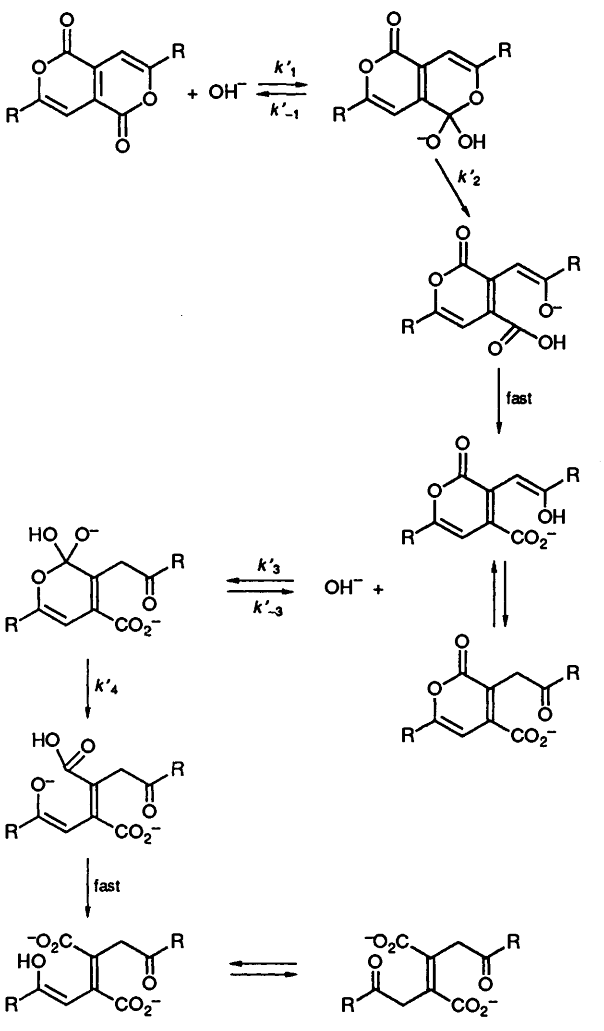
pyranopyrandione system. A Perkin-Elmer FTIR 1650 spectrophotometer was used for the IR spectral measurements and the substrates were studied in a quartz cell at *ca.* 1 × 10^{-3} mol dm^{-3} lactone in spectroscopic grade AnalaR carbon tetrachloride. The bifuranylidenedione and pyranopyrandione have carbonyl stretching frequencies at *ca.* 1782, 1765 and 1743 cm^{-1}, respectively. The former result arises from Fermi resonance and both results agree with the stated structures.[12]

Results and Discussion

The alkaline hydrolysis of both the substituted systems gave biphasic reactions. A very rapid primary reaction was indicated by two factors. Firstly, the absorption at the corresponding λ_{max} decreased almost instantaneously by *ca.* 12–15% on addition of base before the less rapid secondary reaction commenced. Secondly, base equivalent to the substrate concentration was consumed in this step. The less rapid secondary reaction was found to be first-order in base when the initial concentration of base, *b*, minus the substrate concentration, *x*, was used. If the base concentration used was equal to that of the substrate, the less rapid secondary reaction effectively did not occur. The less rapid reaction was found to be first order in substrate and in hydroxide anion. The observed first-order rate coefficients, k_1, in substrate were converted to the second-order rate coefficients, k_2, using eqn. (1), where *b* is the added base concentration and

$$k_2 = k_1/(b - x) \qquad (1)$$

x the substrate concentration. The second-order rate coefficients were calculated by Corbett's method[13] when the excess of base was only two-fold or greater. A reaction pathway is outlined in Scheme 1 for the bifuranylidenediones. A closely analogous pathway is suggested in Scheme 2 for the pyranopyrandiones. The products of the primary hydrolysis may be enolic as the UV–VIS absorption indicates retention of the chromophores. These enols might be expected to be stable because of either intramolecular hydrogen-bonding in the mono-anion or resonance interactions as in tetronic acids[14] and related enols.[15] It was not possible to isolate the intermediate product, which appears to cyclise spontaneously as the acid. The rate determining step for the less rapid reaction is suggested to be k_3' in Scheme 1 or 2, on the basis of studies of the reactivity of other lactones[16] and pseudo-esters.[17] The rate coefficients for these reactions of the substituted substrates of both systems are shown in Table 3. The effects of



Scheme 2

Table 4 The Hammett reaction constant (ρ) for the alkaline hydrolysis of the bifuranylidenediones (**1**) and pyranopyrandiones (**2**) in 70% (v/v) aqueous dioxane at 30.0 °C

System	ρ	$\log k_0$	r	s	n
1	1.902	2.666	0.991	0.128	7
2	1.961	2.082	0.996	0.082	7

[a] s is the standard deviation, r the correlation coefficient and n the number of substituents.

substitution have been successfully assessed by use of the Hammett eqn. (2). The results of these correlations are

$$\log(k/k_0) = \rho\sigma \qquad (2)$$

shown in Table 4. The ρ values of *ca.* 1.9 are clearly in accord with the detailed mechanism suggested. A value of ρ of *ca.* 2.3 can be estimated for both systems on the basis of the ρ value for the alkaline hydrolysis of *meta*/*para*-substituted methyl benzoates under the same conditions[8] and the transmission coefficients tabulated by Bowden.[18] The latter estimate is in reasonable agreement with the ρ values found. The activation parameters for unsubstituted parent substrates are shown in Table 5. The enthalpies of activation are small and the entropies of activation are large and negative compared to those observed for other lactone, pseudo-ester and ester alkaline hydrolyses,[8,16,17] but are consistent with the pathway indicated.

Table 5 Activation parameters for the alkaline hydrolysis of (E)-5,5′-diphenylbifuranylidene-2,2′-dione (**1**, X = H) and 3,7- diphenylpyrano[4,3-*c*]pyran-1,5-dione (**2**, X = H) in 70% (v/v) aqueous dioxane at 30.0 °C[a]

	$\Delta H^{\ddagger}$/kcal mol^{-1}	$\Delta S^{\ddagger}$/cal mol^{-1} K^{-1}
1, X = H	4.9	−29
2, X = H	6.5	−28

[a] Values of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ are considered to be accurate to within ±300 cal mol^{-1} and ±2 cal mol^{-1} K^{-1}, respectively

The lactones studied here all have a '*cis*' conformation, as for other small-ring lactones.[16,17] This appears to increase the initial state energy and is the principal cause of their increased reactivity. A quantitative comparison can be made with the alkaline hydrolysis in 70% v/v aqueous dioxane of coumarin, a benzopyran-2-one. The rate of hydrolysis at 30 °C of the latter compound[19] is *ca.* 300 times slower than the secondary hydrolysis step of the parent pyranopyrandione studied here.

A comparison between the reactivity of the five- and six-membered lactones studied here is particularly valuable. These systems are both fully conjugated unsaturated systems with planar rings. This is in contrast to a number of other five- and six-membered lactone and pseudo-ester systems which are not fully comparable owing to either buckled rings or varying degrees of conjugation, *cf.* references 16 and 17. However, the result in the present study is quite clear. The five-membered ring is significantly more reactive than the six-membered, *i.e.* *ca.* five times at 30 °C for the parent substrates. This arises almost completely from the decreased enthalpy of activation for the former system. The more reactive system does exhibit a smaller ρ value, but the difference does not appear to be significant. The increased reactivity appears to arise from the greater release of ring-strain in forming the transition state for the alkaline hydrolysis of the five- than the six-membered system.[20] The resulting angle strain in the five-membered lactone is *ca.* −51°, and −40° in the tetrahedral intermediate. In the six-membered lactone it is *ca.* +9°, and +20° in the intermediate. The strain in the five-membered ring will be severe, but *decreases* on addition of hydroxide ion. However, in the six-membered ring the strain is not severe and *increases* on addition of hydroxide ion. The discrepancies in the relative reactivity between five- and six-membered systems, in general, appear to result from the lack of strict comparability of the systems in other studies.[17] The results in the present study appear to be due only to angle strain effects, unlike those of previous studies[16] of conformationally mobile systems which have variable torsional strain and steric 'bulk' effects.

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