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REARRANGEMENT OF SUBSTITUTED (*E*)-5,5′-DIPHENYLBIFURANYLIDENEDIONES TO 3,7-DIPHENYLPYRANO[4,3-*c*]PYRAN-1,5-DIONES

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The rate coefficients for the rearrangement of substituted (*E*)-5,5′-diphenylbifuranylidenediones to form the corresponding 3,7-diphenylpyrano[4,3-*c*]pyran-1,5-diones in ethane-1,2-diol at 30.0 °C, catalysed by sodium acetate, were determined. For the unsubstituted dione, the rate coefficients for there arrangement in various alcohols at 30.0 °C, and for three at 59.8 °C, were measured. The reactions were first order in both substrate and acetate anion. Rate coefficients were also measured for the catalysis of the rearrangement of the unsubstituted dione in ethanol and ethane-1,2-diol at 30.0 °C by a series of sodium *meta/para*-substituted benzoates. Brønsted-type correlations for the latter give $\alpha \approx 1.2$. Substrate substitutent effects on the rates of rearrangement of the diones were not marked. A good correlation was found between the rates of rearrangement of the unsubstituted dione and the solvent effect parameter $E_T(30)$. This and other evidence indicated a probable mechanism involving a rapid pre-equilibrium between the substrate diones and the carboxylate anion, followed by the formation of an *s-trans*-enolate anion. The latter rotates to the *s-cis* isomer, which then intramolecularly attacks the second lactone ring. The process is then repeated with the product dione resulting from loss of the carboxylate anion. © 1997 by John Wiley & Sons, Ltd.

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INTRODUCTION

In 1959, it was reported[1] that the pigments, substituted (*E*)-5,5′-diphenylbifuranylidenediones (**1**), described as ‘Pechmann dyes,’[2,3] rearrange into 3,7-diphenylpyrano[4,3-*c*]pyran-1,5-diones (**2**) by heating in alkanediols and alkanetriols, such as ethane-1,2-diol, propane-1,2- or -1,3-diol and butane-1,2,4-triol. Owing to the low solubility of the pigments, the latter solvents were used in combination with a co-solvent, such as nitrobenzene or benzyl alcohol. This transformation had previously been accomplished by alkaline hydrolysis of the five-membered dilactones (**1**), using alcoholic potassium hydroxide, followed by ring closure in an acidic medium.[3] More recently, Rahmani and Crombie[4] studied the rearrangement of two five-membered dilactones to form the corresponding six-membered dilactones and a pathway involving methanolysis was suggested.

The present investigation involved a study of the rearrangement of substituted (*E*)-5,5′-diphenylpyrano[4,3-*c*]pyran-1,5-diones. The kinetics, catalysis, substituent effects, solvent and solvent isotope effects and activation parameters, were investigated in formulating a mechanistic pathway.

EXPERIMENT AND RESULTS

Materials

The methods used for the synthesis of the substituted (*E*)-5,5′-diphenylbifuranylidenediones and 3,7-diphenylpyrano-[4,3-*c*]pyran-1,5-diones have been described previously.[5] Solvents, catalysts and other materials were carefully purified by standard procedures.[6–8]

Kinetic measurements and product analysis

Rate coefficients for the rearrangement of the (*E*)-5,5′-diphenylbifuranylidenediones were determined spectrophotometrically by use of a Perkin-Elmer Lambda 5 UV–visible spectrophotometer. The cell temperature was

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Table 1. Rate coefficients (k_2) for the rearrangement of (*E*)-5,5′-diphenylbifuranylidenedione (**1a**) to 3,7-diphenylpyrano[4,3-*c*]pyran-1,5-dione (**2a**) at 30.0 °C[a,b]

	k_2 ($dm^3 mol^{-1} s^{-1}$)	
Catalyst	In ethanol	In ethane-1,2-diol
Na acetate	0·534	2·84
Na benzoate	0·426	2·00
Na *m*-toluate	0·320	1·59
Na *m*-chlorobenzoate	0·0640	0·450
Na *m*-nitrobenzoate	0·00822	0·0612
Na *p*-methoxybenzoate	0·714	2·62
Pyridine	–	0.260

[a] Rate coefficients were reproducible to $< \pm 3\%$.

[b] The wavelengths used were 500 and 510 nm for ethanol and ethane-1,2-diol, respectively.

controlled to within ±0.05 °C by means of a Churchill thermocirculator. The reactions were followed at suitable wavelengths, which were at or close to λ_{max} for the substrates and are shown in Tables 1–3. The procedure then followed was similar to that described previously.[9] The substrates were studied at 0.5×10^{-4}–2×10^{-4} mol dm^{-3}. The parent solution of the substrates were prepared in dioxane and the kinetic solutions contained 1.7% (v/v) dioxane. The products of the rearrangement of the substrates studied here were confirmed both by isolation in quantitative yield and, spectroscopically, by comparison of the spectrum of the product with that of the isolated reaction product in the solvent system under study. Only in alcoholic solutions, containing a suitable catalyst, was the rearrangement found to give reproducible kinetics and quantitative results. However, if the alkoxide (as the sodium salt) was present as a catalyst, the only process observed was the formation of the diester of 2,3-dibenzoylfumaric acid.[3] The rearrangement itself in alcoholic solution was found to be strongly catalysed by the salts of carboxylic acids and pyridine (see Table 1), but not by *n*-butylamine and aniline. The reaction was observed to be first order in substrate up to 80% of the reaction and was found to be strongly catalysed by acetate anions. At or up to concentrations of acetate anions of 0.5×10^{-3} mol dm^{-3} in ethanol and ethane-1,2-diol, the reaction was first order in acetate anion. Use of lithium acetate or sodium acetate containing or not containing 18-crown-6 gave almost identical rates. At or up to concentrations of benzoate and substituted benzoate anions of 5×10^{-3} mol dm^{-3}, the reactions were first order in the carboxylate anions for *all* substrates and solvents studied. Furthermore, there is *no* significant fall in absorbance of the substrates on initial mixing with the carboxylate anions, which would have occurred if a relatively stable adduct has been rapidly formed. Good isosbestic points were observed for all the rearrangements studied. Tables 1–3 show the rate coefficients for the rearrangements. The activation parameters for the rearrangement of the parent compound at 30.0 °C in three alcohols are shown in Table 4.

Table 2. Rate coefficients (k_2) for the rearrangement of substituted (*E*)-5,5′-diphenylbifuranylidenediones (**1**) to 3,7-diphenylpyrano[4,3-*c*]pyran-1,5-diones (**2**) in ethane-1,2-diol containing sodium acetate at 30.0 °C[a]

Substituent	k_2 ($dm^3 mol^{-1} s^{-1}$)	λ (nm)
H	2·84	510
p-OMe	2·20	520
p-OPh	2·48	530
p-Me	3·16	520
p-Ph	1·92	540
p-Cl	2·90	520
p-Br	2·90	530
m-NO_2	2·98	535

[a] Rate coefficients were reproducible to $< \pm 3\%$.

Table 3. Rate coefficients (k_2) for the rearrangement of (*E*)-5,5′-diphenylbifuranylidenediones (**1a**) to 3,7-diphenylpyrano[4,3-*c*]pyran-1,5-dione (**2a**) in various alcohols containing sodium acetate at 30.0 °C[a]

Alcohol	$10^2 k_2$ ($dm^3 mol^{-1} s^{-1}$)	λ (nm)
Methanol	278 (212)[b]	520
Benzyl alcohol	65·6	510
Ethanol	53·4 (39·0)[b] (692)[c]	500
Ethane-1,2-diol	284 (3460)[c]	510
2-Methoxyethanol	83·2 (1400)[c]	525
Propan-1-ol	38·8	495
Propan-2-ol	9·78	495

[a] See Table 1.

[b] [O-$^2H_1$]Alcohol.

[c] At 59.8 °C.

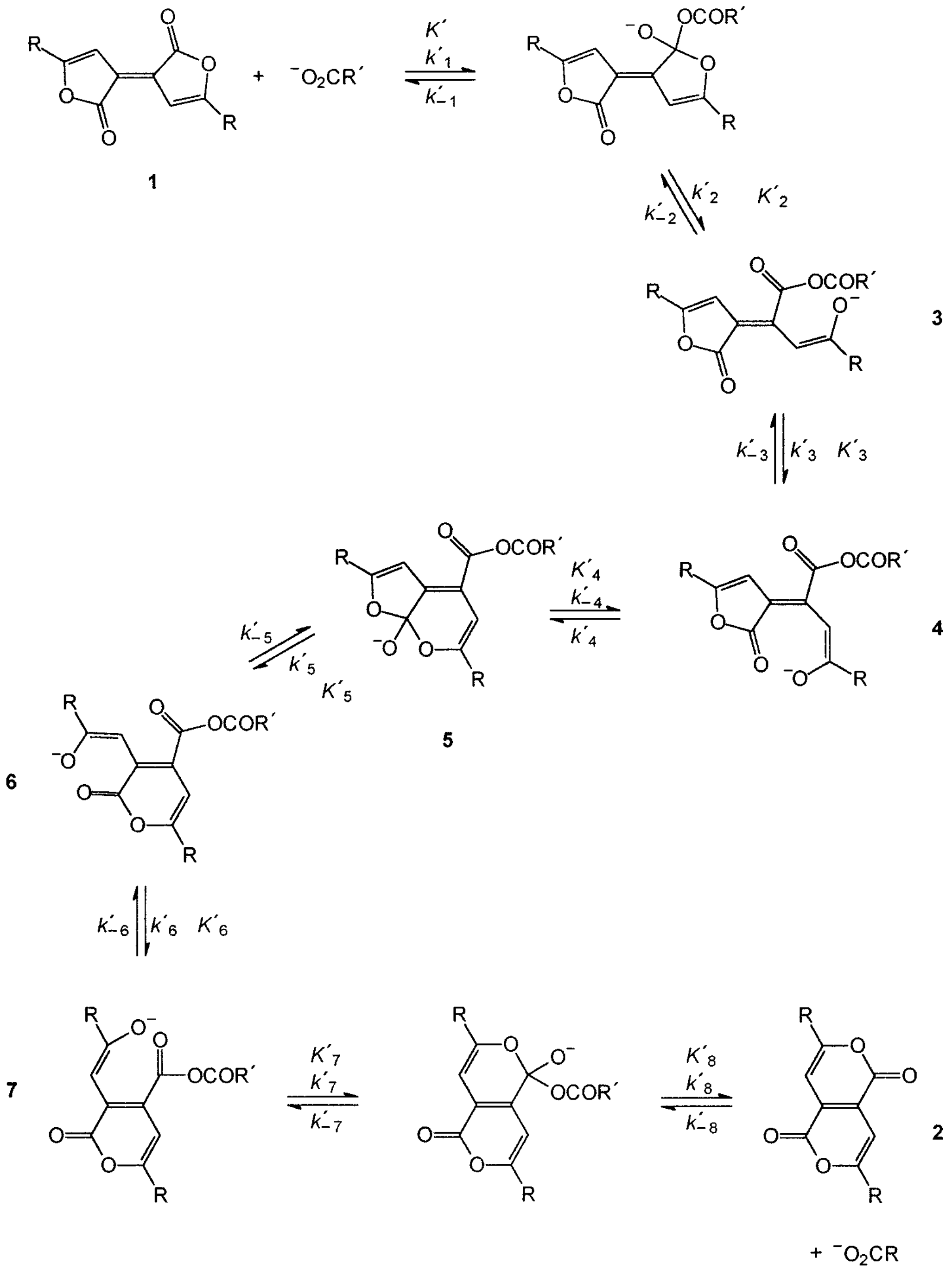
DISCUSSION

A probable mechanistic pathway is shown in Scheme 1 for the rearrangement. The first step is the relatively rapid pre-equilibrium formation of a mixed anhydride, **3**, from the reactive five-membered dilactone and the carboxylate anion. The effect of substituents in the *meta*/*para*-substituted benzoate anions can be correlated using the Hammett equation:

Table 4. Activation parameters for the rearrangement of (*E*)-5,5′-diphenylbifuranylidenediones (**1a**) to 3,7-diphenylpyrano[4,3-*c*]pyran-1,5-dione (**2a**) in ethane-1,2-diol, 2-methoxy ethanol and ethanol at 30.0 °C

Alcohol	$\Delta H^{\ddagger}$ (kcal mol^{-1})[a]	$\Delta S^{\ddagger}$ (cal $mol^{-1} K^{-1}$)[a]
Ethane-1,2-diol	16·2	−3
2-Methoxyethanol	18·4	2
Ethanol	16·6	−5

[a] Values of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ are considered accurate to ±300 cal mol^{-1} and ±1 cal mol^{-1} K^{-1}, respectively.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2
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K′8
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k′−8
+ ⁻O2CR′
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Scheme 1

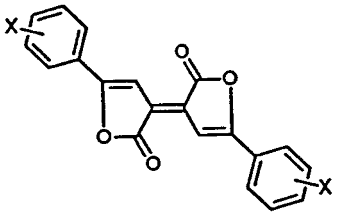
Table 5. Hammett reaction constants (ρ) for the rearrangement of the bifuranylidenediones (**1**) to the pyrandiones (**2**) at 30.0 C[a]

System	ρ	Log k_0	r	s	n
m/*p*-Substituted benzoates as catalysts in ethane-1,2-diol	−1·677	0·119	0·972	0·236	5
As above in ethanol	−1·991	−0·565	0·984	0·208	5
5,5′-Di (*m*/*p*-substituted phenyl) diones in ethane-1,2-diol catalysed by acetate	0·149	0·415	0·554	0·091	8

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

$$\log (K/K_0) \text{ or } (k/k_0) = \rho \qquad (1)$$

The correlation is satisfactory, as shown in Table 5, with a ρ value of about −1.7 for ethane-1,2-diol and -2.0 for ethanol. These results can be related to the ionization of these acids measured in the same solvent systems,[10] having ρ values for about 1.5 for both ethane-1,2-diol and ethanol. A Brønsted-type coefficient, α, of about 1.1 and 1.3 can be calculated from the ratio $-(\rho_{cat}/\rho_{ioniz})$.[11] Whereas Brønsted coefficients for acid- and base-catalysed reactions are generally between zero and unity, the slopes of the relationship between nucleophilic rate coefficients and ionization constants are not so limited.[12] A relevant reaction for comparison is the nucleophilic catalysis (pyridines and other bases) of the hydrolysis of *p*-nitrophenyl acetate in water at 25.2 °C.[12] The value of α for the latter reaction is 1.62 in water and the reaction gives first the reactive intermediates, the *N*-acetylpyridinium cations. Such hydrolysis reactions are also catalysed by acetate anions and then can proceed *via* acetic anhydride.[12] Hence the present results indicate the likelihood of relatively rapid formation of the adduct in a pre-equilibrium step. The Brønsted coefficients of greater than unity suggest that the transition state for the reaction is at or after the formation of the intermediate **3**. The effect of the di-*meta*-/*para*-substitution in the substrate can also be assessed using the Hammett equation (1). The result of the correlation is shown in Table 5. The latter is very poor and is typical for Hammett relations where ρ is close to zero.[13] In the second step, the enolate anion is formed by fission of the first strained five-membered lactone ring which will then suffer rotation about the single bond from the *s-trans* (**3**) to the *s-cis* (**4**) isomer. The next step is the intramolecular nucleophilic attack of the *s-cis*-enolate anion on the second five-membered lactone ring to form the second tetrahedral intermediate **5**. This process is exactly analogous to several neighbouring group participation reactions.[14]



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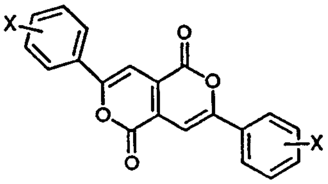

2

The intermediate **5** should be unstable as it has a fused six- and five-membered bicyclic ring structure, which will be strained. This should collapse rapidly to the *s-trans* isomer (**6**). A passage over a rotational barrier then gives the *s-cis* isomer (**7**). This is followed by an intramolecular attack of the *s-cis*-enolate anion on the mixed anhydride. The tetrahedral intermediate formed will rapidly lose the original nucleophilic carboxylate anion to form the fused six- and six-membered bicyclic structure or product **2**.

Studies of the effect of solvent on the rates were very illuminating. As shown in Table 3, the rate increases by about a factor of about 30 on going from the less polar propan-2-ol to the more polar ethane-1,2-diol. The linear correlation between log k_1 and $E_T(30)$[6] is good, with a correlation coefficient of 0.954 and a slope of 0.17 (±0.02). This clearly indicates the importance of solvation in stabilizing the transition state in comparison with the initial state. Enolates and similar anionic species require protic solvation for stabilization.[15] The kinetic solvent isotope effect, k_{ROH}/k_{ROD}, for both methanol and ethanol is about 1.3. This is in accord with the expected change in the hydrogen-bonding solvating capacity of the solvents arising from replacing OH and OD.[16] Hence, this excludes any primary isotope effects on the rate-determining step.

The activation parameters for the rearrangement reaction of the parent compound in the three alcoholic solvents shown in Table 4 are consistent with a bimolecular mechanistic pathway, i.e. a rate-determining unimolecular process following a relatively rapid pre-equilibrium bimolecular process. However, the values for the entropies of activation are close to zero and strongly suggest a rate-determining step involving a process releasing strain and increasing freedom, i.e. k'_2 or k'_3 in Scheme 1.

The drive for the overall rearrangement of the five-membered dilactone **1**, to the six-membered dilactone, **2**, is the greater thermodynamic stability of the bicyclic six- and six-membered fused ring system, **2**, which is fully coplanar and almost strain free.[17]

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