

# Reactions of carbonyl compounds in basic solutions. Part 23.<sup>1</sup> The mechanism of the base-catalysed ring fission of 2,2-dihydroxyindane-1,3-diones

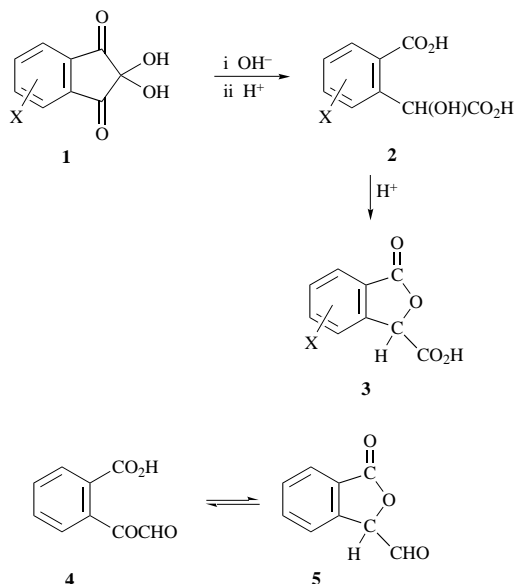
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The base-catalysed ring fission of a series of substituted 2,2-dihydroxyindane-1,3-diones and phenalene-1,3-dione has been studied in 30% (v/v) dioxane–water. The reaction proceeds in two distinct steps. The first is a relatively fast base-catalysed ring fission to give substituted *o*-carboxyphenylglyoxals, and the second is a rearrangement of the latter resulting in formation of substituted *o*-carboxymandelic acids. Rate coefficients for the ring fission of a limited series of substrates have been determined at 25.0 °C. The reaction is first order in the mono-anion of the substrate alone. The Hammett reaction constants,  $\rho$ , have been obtained from both the kinetic and product studies. The rate- and product-determining step appears to be an intramolecular nucleophilic attack. The rate- and product-determining step appears to be determined for all substrates at 25.0, 35.0 and 45.0 °C. The activation parameters have been calculated. The kinetic solvent isotope, solvent and salt effects have been studied. The effects of the 5-substituted and 5,6-disubstituents on the rates have been correlated using a modified Hammett equation giving a reaction constant,  $\rho$ , equal to 3.4 at 25 °C.

The benzilic acid and related rearrangements were reviewed in 1960 by Selman and Eastham.<sup>2</sup> These included the intramolecular Cannizzaro-type reaction of phenylglyoxal<sup>3</sup> and the base-catalysed rearrangement–fission of 1,3-diphenylpropane-1,2,3-triones.<sup>4,5</sup> However, in 1910, Ruhemann<sup>6</sup> had found that indane-1,2,3-trione, as the hydrate (ninhydrin) **1**, rearranged in base to give *o*-carboxymandelic acid **2** (isolated as its lactone **3**). More recently, the kinetics of this reaction were studied using polarography<sup>7</sup> and a pathway involving *o*-carboxyphenylglyoxal **4/5** as an intermediate was suggested. This suggestion



had already been made by Ruhemann.<sup>6</sup> A closely related pathway has been offered for the reaction of **1** with cyanide.<sup>8</sup>

The present study describes a detailed investigation of base-catalysed ring fission of a series of substituted 2,2-dihydroxyindane-1,3-diones. The products of the fission have been determined and possible intermediates examined. The rates of the base-catalysed ring fission and rearrangement, activation

parameters, substituent, salt, solvent and solvent isotope effects are reported. The present study, together with the following Parts 24 and 25, present an attempt to elucidate the pathways for base-catalysed ring fission of 1,2-dicarbonyl and 1,2,3-tricarbonyl compounds, as well as the factors controlling their modes of reactivity.

## Results and discussion

### Acidity of the hydrates

The 2,2-dihydroxy 1,3-diones are *gem*-diols and are considerably more acidic than 1,2-glycols. It is possible to estimate the  $pK_a$  in water of 2,2-dihydroxyindane-1,3-dione **1** as 8.8<sub>s</sub>, using the relation (1) for *gem*-diols and  $\sigma^*$  for PhCO equal to 2.2.<sup>9</sup>

$$pK_a = 14.4 - 1.42 \sum \sigma^* \quad (1)$$

The  $pK_a$  of **1** has been reported to be 8.6 from polarographic studies,<sup>7</sup> with the dihydrate, 1,1,2,2-tetrahydroxyindan-3-one, being considered to be a significantly weaker acid. For the kinetics studied here, the base concentrations were sufficient to ionise almost completely the *gem*-diols.

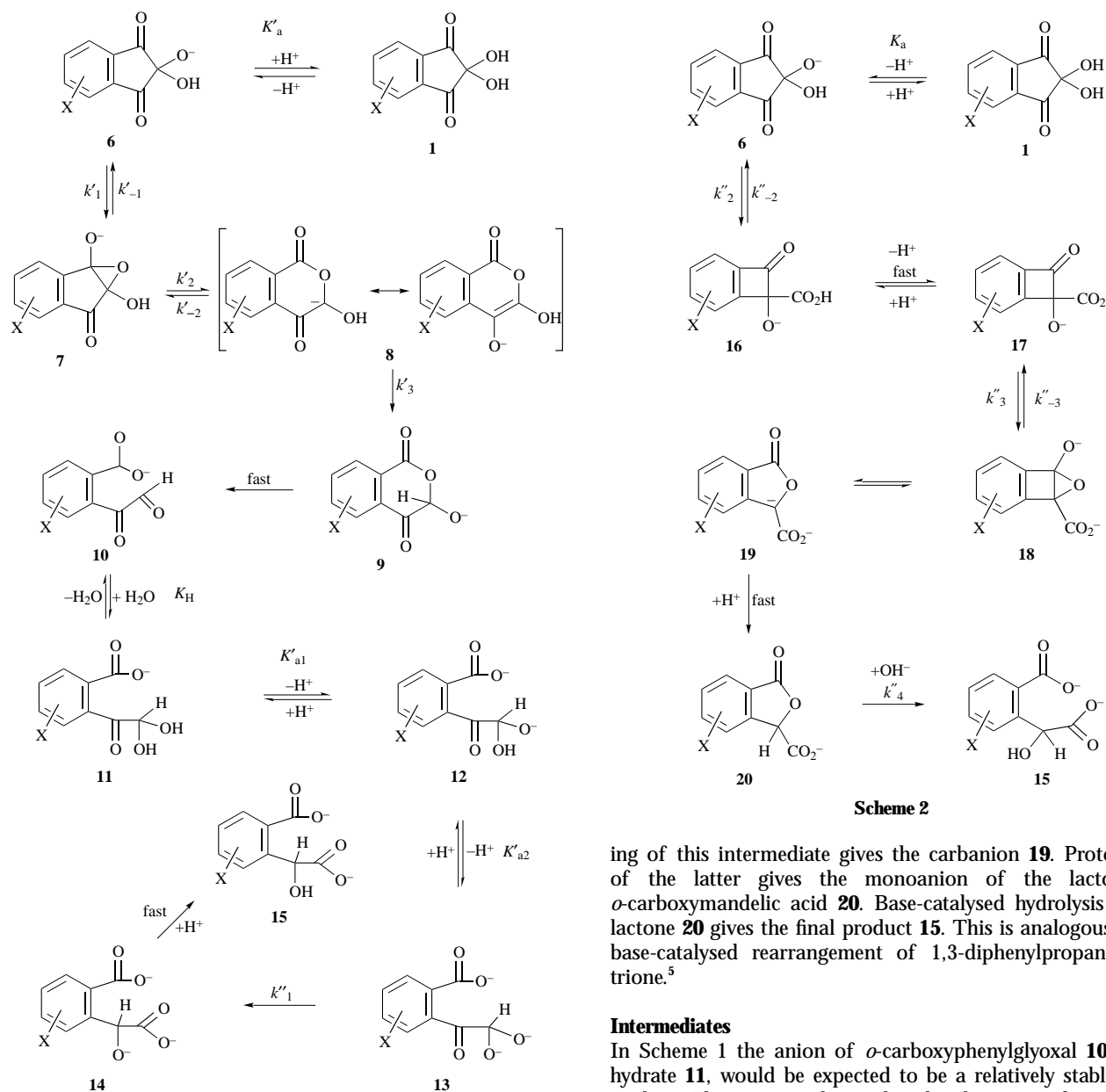
### The base-catalysed ring fission and rearrangement

Two possible mechanistic schemes are shown in Schemes 1 and 2. Scheme 1 shows a pathway involving intramolecular nucleophilic attack within the anion **6** to form the fused oxirane **7**. Ring opening of this intermediate gives the carbanionic intermediate **8**. These processes have analogies with both the reaction of **1** with nitroalkanes<sup>10</sup> and the reaction of 1,2-dicarbonyl compounds with cyanide.<sup>11,12</sup> Proton exchange in the intermediate **8** is followed by ring-opening of the semi-acetal anion **9**, resulting in the formation of the monoanion of *o*-carboxyphenylglyoxal **10**. Compound **10** may be regarded as a relatively stable intermediate which will suffer an intramolecular Cannizzaro-type reaction catalysed by base to give the dianion of *o*-carboxymandelic acid **15** as the final product, *cf.* ref. 3. Scheme 2 shows a pathway which is essentially a benzilic acid-type rearrangement of the type employed by related 1,2-dicarbonyl and 1,2,3-tricarbonyl compounds.<sup>2-4</sup> The

**Table 1** Rate coefficients ( $k_1$  and  $k_2$ ) for the base-catalysed ring fission and rearrangement of substituted 2,2-dihydroxyindane-1,3-diones in 30% (v/v) dioxane–water ( $\mu = 0.1 \text{ mol dm}^{-3}$ )

Substituent(s)		Ring fission <sup>a</sup> $k_1/10^{-2} \text{ s}^{-1}$ at 25 °C	Rearrangement <sup>b</sup> $k_2/10^{-2} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$			$\lambda/\text{nm}^c$
5-	6-	at 25.0 °C	at 25.0 °C	at 35.0 °C	at 45.0 °C	
H	H	5.00	5.89 (2.14) <sup>d</sup>	11.2	21.2	230, 246
CH <sub>3</sub>	H	<i>e</i>	1.29	2.82	5.77	—, 234
OCH <sub>3</sub>	H	<i>e</i>	0.820	1.86	4.08	—, 240
Cl	H	11.0	45.4	87.7	161	235, 223
CH <sub>3</sub>	CH <sub>3</sub>	<i>e</i>	0.408	0.944	2.12	—, 241
OCH <sub>3</sub>	OCH <sub>3</sub>	<i>e</i>	0.129	0.313	0.746	—, 255
Cl	Cl	21.8	237 (87.8) <sup>d</sup>	450	796	240, 240
Benzo[ <i>f</i> ]		<i>e</i>	3.51	7.61	15.6	—, 269
Phenylene-		1.22	89.9	236	584	220, 324
1,3(2 <i>H</i> )-dione						

<sup>a</sup> Rate coefficients were reproducible to  $\pm 6\%$ . <sup>b</sup> Rate coefficients were reproducible to  $\pm 3\%$ . <sup>c</sup> Wavelengths used to monitor the ring fission and rearrangement reaction, respectively. <sup>d</sup> In 30% (v/v) dioxane–deuterium oxide. <sup>e</sup> Rate coefficients could not be obtained (see text).



monoanion **6** suffers ring contraction by migration of the aryl group to form the benzocyclobutanone **16**. This is followed by rapid ionisation of the carboxylic acid to form **17** and then intramolecular attack to give the fused oxirane **18**. Ring open-

ing of this intermediate gives the carbanion **19**. Protonation of the latter gives the monoanion of the lactone of *o*-carboxymandelic acid **20**. Base-catalysed hydrolysis of the lactone **20** gives the final product **15**. This is analogous to the base-catalysed rearrangement of 1,3-diphenylpropane-1,2,3-trione.<sup>5</sup>

#### Intermediates

In Scheme 1 the anion of *o*-carboxyphenylglyoxal **10**, or its hydrate **11**, would be expected to be a relatively stable intermediate. This was not observed, isolated or trapped in previous studies.<sup>6–8</sup> Phenylglyoxals have been shown to readily undergo intramolecular Cannizzaro-type reactions to form the monoanions of mandelic acids in base.<sup>3,4</sup> *o*-Carboxyphenylglyoxal has been prepared directly as the product of ozonolysis of 1,4-naphthoquinone.<sup>13</sup>

In this study, the kinetics of the base-catalysed fission of the

**Table 2** Product ratios, *ratio*, for the base-catalysed ring fission and activation parameters for the base-catalysed rearrangement of substituted 2,2-dihydroxyindane-1,3-diones in 30% (v/v) dioxane–water at 30 °C ( $\mu = 0.1 \text{ mol dm}^{-3}$ )

Substituent(s)		Rearrangement <sup>a</sup>		Ring fission product ratio, <sup>b</sup> ratio
5-	6-	$\Delta H^\ddagger/\text{kcal mol}^{-1c}$	$\Delta S^\ddagger/\text{cal mol}^{-1} \text{ K}^{-1c}$	
H	H	11.5	–26	1
CH <sub>3</sub>	H	13.5	–22	0.80 <sub>5</sub>
OCH <sub>3</sub>	H	14.5	–19	0.30 <sub>5</sub>
Cl	H	11.3	–22	0.62
CH <sub>3</sub>	CH <sub>3</sub>	14.9	–20	1
OCH <sub>3</sub>	OCH <sub>3</sub>	16.0	–18	1
Cl	Cl	10.8	–21	1
Benzo[ <i>f</i> ]		13.5	–20	1
Phenylene-1,3(2 <i>H</i> )-dione		17.0	–2	1

<sup>a</sup> Values of  $\Delta H^\ddagger$  and  $\Delta S^\ddagger$  are considered accurate to within  $\pm 300 \text{ cal mol}^{-1} \text{ K}^{-1}$  and  $\pm 1 \text{ cal mol}^{-1} \text{ K}^{-1}$ , respectively. <sup>b</sup> See text. <sup>c</sup>  $1 \text{ cal} = 4.184 \text{ J}$ .

**Table 3** Rate coefficient ( $k_2$ ) for the base-catalysed rearrangement of 2,2-dihydroxyindane-1,3-dione in aqueous dioxane at 25.0 °C ( $\mu = 0.1 \text{ mol dm}^{-3}$ )<sup>b</sup>

Volume (%) dioxane	$k_2/10^{-2} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$
0 <sup>a</sup>	5.15
10	5.03
30	5.89 (10.2) <sup>c</sup> (11.0) <sup>d</sup>
50	13.6
70	120

<sup>a</sup> 0.5% (v/v) dioxane–water. <sup>b</sup> See Table 1. <sup>c</sup>  $\mu = 0.5 \text{ mol dm}^{-3}$ . <sup>d</sup>  $\mu = 1.0 \text{ mol dm}^{-3}$ .

substituted 2,2-dihydroxy 1,3-diones has been found to be biphasic. First, there is a very rapid reaction to form a relatively stable intermediate. The UV–VIS spectra of the intermediate product for **1** is almost identical with that of *o*-carboxyphenylglyoxal under the same conditions. This first reaction is first order in the substrate (mono-anion of *gem*-diol) and zero order in base. Secondly, there is a fast, but relatively slow, reaction to form the final products of the reaction, the dianion of the corresponding *o*-carboxymandelic acids. The second reaction is first order both in the substrate and in base. The rate of this reaction for **1** is identical with that of *o*-carboxyphenylglyoxal under the same conditions. Table 1 shows the rate coefficients for the base-catalysed ring fission and rearrangement in 30% (v/v) dioxane–water, with the activation parameters and solvent and salt effects on the rates of rearrangement shown in Tables 2 and 3, respectively.

In Scheme 2 the monoanion of the lactone of *o*-carboxymandelic acid **20** could be a relatively stable intermediate. The isolated product, after treatment with acid, is the lactone itself. This lactone is rapidly hydrolysed in aqueous base with  $k_1$  equal to *ca.*  $1.23 \text{ s}^{-1}$  in water at  $0.01 \text{ mol dm}^{-3}$  base at 25 °C. Thus, if formed as an intermediate, **20** would not be observed.

The evidence appears to be unequivocally in favour of Scheme 1.

### Rates of base-catalysed ring fission

Owing to biphasic kinetics, rapidity of reactions and spectral changes, it was only possible to measure securely the rate coefficients for the base-catalysed ring fission of the four most reactive substrates, *i.e.* the unsubstituted, 5-chloro- and 5,6-dichloro-2,2-dihydroxyindane-1,3-diones and 2,2-dihydroxyphenylene-1,3-dione, in 30% (v/v) dioxane–water at constant ionic strength ( $\mu = 0.1 \text{ mol dm}^{-3}$ ) at 25.0 °C. The reactions were first order in the mono-anion of the substrate. The rates of reaction are accelerated by electron-withdrawing substituents. The six-membered ring 2,2-dihydroxyphenylene-1,3(2*H*)-dione reacts significantly slower than the five-membered ring 2,2-dihydroxyindane-1,3-dione **1**. Angle strain in the five-membered cycle system (*ca.*  $+48^\circ$ ) is much greater than that in the six-membered cyclic system (*ca.*  $-12^\circ$ ). As the ring fission

**Table 4** Hammett reaction constants ( $\rho$ ) for the base-catalysed reactions of substituted 2,2-dihydroxyindane-1,3-diones

	$\rho$	$\log k_0$	$r$	$s$	$n$
Ring fission					
5-Substituent and 5,6-disubstituent with $\sigma_p$ and $2\sigma_p$	0.857	–1.203	0.999	0.035	3
5-Substituent and 5,6-disubstituent with $\sigma_m$ and $2\sigma_m$	1.409	–1.203	0.999	0.058	3
5-Substituent product ratios with ( $\sigma_p - \sigma_m$ )	1.335	0.007	0.994	0.105	4
Rearrangement					
Mono-substituents with $\sigma_p$	3.580	–1.199	0.996	0.229	4
Disubstituents with $2\sigma_p$	3.380	–1.186	0.999	0.120	4
Mono-substituents and disubstituents with $\sigma_p$ and $2\sigma_p$	3.362	–1.191	0.998	0.108	7
(Hydration vs. rearrangement)	0.380	–1.642	0.971	0.031	8

<sup>a</sup>  $s$  is the standard deviation,  $r$  the correlation coefficient and  $n$  the number of substituents studied.

results in open-chain systems, the relative ring strain would appear to be the main source for this rate difference.

### Kinetic substituent effects

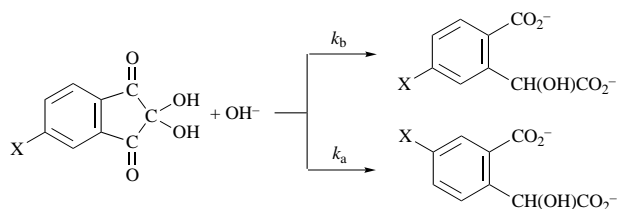
The Hammett equation (2) is usually employed in the quanti-

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

tative assessment of *meta/para*-substituent effects in aromatic systems.<sup>14</sup> For 2,2-dihydroxyindane-1,3-diones, the situation is more complex for 5- or 6-substituents, which could be considered to be both *meta*- and *para*-substituents for reactions in the side-chain. Having results for only three relevant substrates, it is only possible to make preliminary correlation studies with either  $\sigma_p$  and  $2\sigma_p$ , for the 5-substituted and the identically 5,6-disubstituted, respectively, or, similarly,  $\sigma_m$  and  $2\sigma_m$ . The correlations given are shown in Table 4 and are good with  $\rho$  equal to *ca.* 0.9 or 1.4 (see further below).

### Product substituent effects

The final isolated reaction products for base-catalysed ring fission of the substituted 2,2-dihydroxyindane-1,3-diones are the corresponding lactones of the substituted *o*-carboxymandelic acids **3**. For the unsubstituted and identically disubstituted substrates, there is only one product. For the monosubstituted substrates there are two possible products, as shown in Scheme 3, *i.e.* the di-anions of the 5- and 4-substituted 2-carboxymandelic acids. The product ratios, *ratio*, of the corresponding lactones, *i.e.* the 1,3-dihydro-3-oxoisobenzofuran-1-carboxylic acids, were measured using <sup>1</sup>H NMR spectroscopy and are shown in Table 2. Thus, *ratio* is equal to the ratio of 4-substituted to that of 5-substituted *o*-carboxymandelic acid,  $x_4/x_5$ . These results



Scheme 3

are of importance as they identify the point of cleavage of the substrate. The 5-substituted product predominates in all cases. The Wegscheider principle<sup>15</sup> relates the ratio of two products formed in irreversible, simultaneous reactions to their rates of formation as shown in eqn. (3). If the Hammett equation is

$$x_4/x_5 = k_a/k_b \text{ or } \log(x_4/x_5) = \log(k_a/k_b) \quad (3)$$

applied to both these processes and the reaction constants for both process forming products are the same, eqn. (4) results, cf.

$$\log(k_b/k_H) = \rho\sigma_m \text{ and } \log(k_a/k_H) = \rho\sigma_p \quad (4)$$

ref. 16. Substituting in eqn. (3) the values of  $\log k_b$  and  $\log k_a$  derived from eqn. (4) gives the final relation, eqn. (5). The

$$\log(x_4/x_5) \text{ or } \log \text{ ratio} = \rho(\sigma_p - \sigma_m) \quad (5)$$

correlation between  $\log \text{ ratio}$  and  $(\sigma_p - \sigma_m)$  is very good as shown in Table 4. The reaction constant,  $\rho$ , equal to *ca.* 1.3 refers to the ring fission product-determining step. The latter process would be the formation of the anionic oxirane **7** from the anion **6**. Model processes, which enable an estimate for  $\rho$  for the latter reaction, would be the development of a negatively charged tetrahedral intermediate for alkaline hydrolysis of suitable esters. For **6** passing to **7**, this is the difference between the  $\rho$  for alkaline hydrolysis of methyl benzoates (2.07 in 40% aqueous dioxane at 20 °C)<sup>17</sup> and of methyl phenylacetates. The latter can be calculated using the transmission coefficient for a methylene group<sup>18</sup> (0.58) as shown in eqn. (6). The estimate of

$$\rho = 2.07 (1.0 - 0.58) = 0.9 \quad (6)$$

0.9 is in reasonable agreement, considering the uncertainties, with the observed value of 1.3. The observed  $\rho$  values for the kinetic and product determining steps are very similar and it appears likely that they relate to the same process, *i.e.*  $k'_1$  in Scheme 1.

#### Rates of base-catalysed rearrangement

The rate coefficients for the base-catalysed rearrangement in 30% (v/v) dioxane–water at constant ionic strength ( $\mu = 0.1 \text{ mol dm}^{-3}$ ) are shown in Table 1. The reported kinetic studies for the ring fission in water of **1** using a polarographic method<sup>7</sup> agree well with the present studies for the rearrangement. The products of the reaction were the dianions of the corresponding substituted *o*-carboxymandelic acids. The reactions were found to be strictly first order in the substrates, the *o*-carboxyphenylglyoxals, *i.e.* the conjugate base of the monoanionic hydrate **12**, and first order in base. The trends in the rates clearly indicate that the rates of reaction are accelerated by electron-withdrawing and retarded by electron-releasing substituents. The fused benzo[*f*] substituent results in a small decrease in the rate resulting from a modest electron-withdrawing resonance effect. 8-Carboxy-1-naphthylglyoxal reacts very much faster than *o*-carboxyphenylglyoxal (see below).

#### Activation parameters

The activation parameters for the base-catalysed rearrangement

are shown in Table 2. These values are consistent with a bi-molecular reaction. In general, electron-withdrawing groups decrease and electron-releasing groups increase  $\Delta H^\ddagger$ . The faster rate for 8-carboxy-1-naphthylglyoxal results from a greatly reduced negative  $\Delta S^\ddagger$  value of  $-2 \text{ cal mol}^{-1} \text{ K}^{-1}$  coupled with a significantly increased  $\Delta H^\ddagger$  value. This suggests a transition state for this compound involving very favourable stereochemistry, but unfavourable electrostatic and steric interactions. This type of behaviour has been found in 1,8-disubstituted systems.<sup>19,20</sup>

#### Kinetic solvent isotope, solvent and salt effects

The kinetic solvent isotope effects,  $k_2^{\text{H}_2\text{O}}/k_2^{\text{D}_2\text{O}}$ , for the unsubstituted and 5,6-dichloro substrates are both *ca.* 0.37 at 25 °C (see Table 1). Thus, no significant, detectable primary isotope effect occurs. Values of  $k_2^{\text{H}_2\text{O}}/k_2^{\text{D}_2\text{O}}$  have been found for the base-catalysed ring fission of benzocyclobutenedione in water at 25 °C,<sup>21</sup> for the benzoic acid rearrangement in 2:1 dioxane–water at 50 °C<sup>22</sup> and for alkaline hydrolysis of methyl benzoate in 70% aqueous dioxane at 25 °C<sup>23</sup> to be 0.58, 0.54 and 0.87, respectively. Such results have been ascribed to the greater basicity and nucleophilicity of deuteroxide anions in  $\text{D}_2\text{O}$ , than of hydroxide anions in  $\text{H}_2\text{O}$ . The reason for the significantly reduced ratio found in this study probably arises from the dianionic initial and transition states in which the solvation effects underlying the kinetic solvent isotope effects are approximately double those observed for monoanionic systems.<sup>24</sup>

The effect of dioxane content on the rates of rearrangement are shown in Table 3, together with the effect of increasing ionic strength. No simple relations between solvent effects and rates exist. However, the dramatic increase in rate with increasing dioxane content would be that expected from the formation of dianionic transition state from two monoanions as an initial state with the greatly decreased relative permittivity of the medium as dioxane content increases.<sup>25</sup> This is quite unlike and opposite to the changes observed for the reaction of dipolar molecules such as methyl benzoate<sup>26</sup> and benzocyclobutenedione<sup>21</sup> with hydroxide anions in aqueous dioxane. The significant increases in rate observed for increased ionic strength of the medium clearly indicate a positive primary salt effect.<sup>27</sup> This appears to indicate a rate-determining step having a transition state with a dianionic structure formed from two monoanions. Comparable effects have been observed for the intramolecular Cannizzaro reaction of biphenyl-2,2'-dicarbaldehyde<sup>28</sup> and the benzoic acid rearrangement of 2-carboxybenzil,<sup>29</sup> both of which involve the formation of a dianion from two monoanions.

#### Kinetic substituent effects

As ring fission has already occurred, the modified Hammett equation suggested by Jaffé<sup>30</sup> for transmission *via* two links is not applicable. It is just possible that a polar effect could be transmitted *via* the 2-carboxylate group, but this is unlikely here. As in our investigation of the uncatalysed hydration of substituted indane-1,2,3-triones,<sup>31</sup> correlations of identical disubstituents using  $\sigma_m + \sigma_p$  are very poor, as is that of mono-substituents using  $\sigma_m$ . Again, correlations of mono-substituent effects with  $\sigma_p$  and identical disubstituent effects with  $2\sigma_p$  are very successful, as shown in Table 4. Similar behaviour was so found for the base-catalysed ring fission of benzocyclobutenediones.<sup>21</sup> A possible cause for this behaviour has been discussed previously.<sup>31</sup> 1,2-Dicarbonyl substitution in a benzene ring may result in powerful cross-conjugation effects with substituents so modifying the expected substituent effects. Furthermore, a plot of  $\log k_1$  for hydration of the substituted indane-1,2,3-triones in 96.7% aqueous dioxane at 25 °C *versus*  $\log k_2$  for the rearrangement reaction in 30% aqueous dioxane at 25 °C is linear with a correlation coefficient of 0.971 (see Table 4), showing that substituents behave very similarly in

**Table 5** The physical constants of the previously unreported substituted 1,3-dihydro-3-oxoisobenzofuran-1-carboxylic acids

Substituents			Found (%)			Calc. (%)			
5-	6-	Mp/ °C	C	H	Other	Formula	C	H	Other
CH <sub>3</sub>	CH <sub>3</sub>	188–190 <sup>a</sup>	64.3	4.7		C <sub>11</sub> H <sub>10</sub> O <sub>4</sub>	64.1	4.9	
OCH <sub>3</sub>	OCH <sub>3</sub>	200–203 <sup>b</sup>	55.1	4.2		C <sub>11</sub> H <sub>10</sub> O <sub>6</sub>	55.5	4.2	
Cl	Cl	194–196 <sup>a</sup>	43.6	1.4	28.0(Cl)	C <sub>9</sub> H <sub>4</sub> Cl <sub>2</sub> O <sub>4</sub>	43.8	1.6	28.7(Cl)

<sup>a</sup> Colourless prisms. <sup>b</sup> Colourless crystals.

both reactions. This is a surprising result as ring fission has already occurred for the substrates of the rearrangement. However, the mono-substituted 2-carboxyphenylglyoxals are a mixture of 4- and 5-substituted compounds. Thus, the reaction constant,  $\rho$ , for the base-catalysed rearrangement was found to be *ca.* 3.4 in 30% aqueous dioxane at 25 °C and indicates the size and position of the charge developed in the transition state, compared to the initial state.<sup>32</sup> Comparisons with other systems must be done with care as these may have been studied in different solvent systems and at different temperatures. The same reaction for a series of substituted phenylglyoxals in water at pH 12 and 25 °C gave a  $\rho$  value of 2.0.<sup>36</sup> The base-catalysed ring fission of benzocyclobutenediones in water at 25 °C<sup>21</sup> and the cyanide-catalysed cleavage of benzils in alcoholic solutions at 30 °C<sup>12</sup> gave  $\rho$  values equal to *ca.* 3.7 and 3.4<sub>5</sub>, respectively. However, the equilibria addition of hydroxide anions to benzaldehydes in water at 25 °C had a  $\rho$  value equal to 2.2<sup>33</sup> or 2.8,<sup>34</sup> whereas, the alkaline hydrolysis of ethyl or methyl benzoates in water at 25 °C<sup>35</sup> and 40% aqueous dioxane at 20 °C<sup>30</sup> had  $\rho$  values equal to 1.3 and 2.1, respectively. Thus, the  $\rho$  values observed here indicate that the negative charge in the transition state must be developed close to the substituted phenyl group a transition state close to **14** in Scheme 1, *cf.* ref. 3.

### Mechanistic pathway

The evidence indicates that the pathway for the base-catalysed ring fission of the 2,2-hydroxy 1,3-diones is that shown in Scheme 1. The rate-determining step for the ring fission process, with a transition state close to the intermediate **7**, appears to be  $k_1$  in Scheme 1. The product-determining step, where dichotomy can exist, would be the same as the latter. The relative ease of the two types of pathways available for such base-catalysed fission reactions, *i.e.* the intramolecular nucleophilic attack as in Scheme 1, *cf.* ref. 21, and the benzylic acid rearrangement, with ring contraction, as in Scheme 2, *cf.* ref. 36, can be considered. The switch is between a 1,2-intramolecular nucleophilic attack of an alkoxide anion on a carbonyl group carbon and a 1,2-migration of an aroyl group to a carbonyl group carbon. Obviously, there are important stereochemical demands on the nucleophilic attack and migration<sup>37</sup> which are more difficult to satisfy when the systems are constrained in a ring system. It would appear that the stereochemistry of the systems studied here allows the intramolecular attack to proceed from a favourable attack angle, *cf.* ref. 37. The intramolecular rearrangement,<sup>34</sup> following the ring fission, for the system under study is a facile process as noted for a range of intramolecular Cannizzaro-type reactions, *e.g.* ref. 28.

## Experimental

### Materials

The 2,2-dihydroxy 1,3-diones and the 1,2,3-triones were prepared and/or purified as described previously.<sup>31</sup> *o*-Carboxyphenylglyoxal was prepared by the ozonolysis of 1,4-naphthoquinone.<sup>13</sup> Pure phenylglyoxal, mandelic and benzoic acids were obtained commercially.

Inorganic salts were of analytical grade and were used with-

out further purification. The solvents were carefully purified by standard methods<sup>38</sup> and stored as described previously.<sup>31</sup>

### Measurements

Rate coefficients for the base-catalysed reactions were determined spectrophotometrically by use of a Perkin-Elmer lambda 16 UV-VIS spectrometer. A Haake thermostatted water circulating bath was used to control the temperature of the cell to  $\pm 0.05$  °C. The procedure was that described previously.<sup>39</sup> The reactions were followed at suitable wavelengths, as shown in Table 1. These were normally those having the greatest differences between the 2,2-dihydroxy 1,3-diones and the products. Rate coefficients were measured at least twice. The reactions were strictly first order in the substrates. The ionic strength was maintained at 0.1 mol dm<sup>-3</sup> using sodium chloride. The substrate concentration was  $1.5 \times 10^{-5}$ – $1.5 \times 10^{-4}$  mol dm<sup>-3</sup> and the base concentrations  $1.5 \times 10^{-4}$ – $1 \times 10^{-1}$  mol dm<sup>-3</sup>, at least a ten-fold excess of base being used. The reactions were found to be either zero order or first order in base, with due allowance for that used in fully ionising the substrates. The same kinetics were obtained if either the 2,2-dihydroxy 1,3-diones or 1,2,3-triones were used as substrates as the latter were very rapidly converted into the former on addition of base. Use of aqueous dioxane as the reaction solvent was required due to the restricted solubility of certain substrates in water.

### Product analysis

The final products of the base-catalysed ring fission reactions of the substituted 2,2-dihydroxyindane-1,3-diones were shown to be quantitatively the dianions of the corresponding *o*-carboxymandelic acids by isolation of the corresponding lactones and UV spectral comparison with the product of hydrolysis of the lactones. In general, the products of the kinetic runs or preparative studies were isolated by acidification and extraction with diethyl ether. After isolation, the lactones were recrystallised from toluene. The same procedures gave the lactone derived from 2,2-dihydroxyphenalene-1,3-dione. The products had either mps in good agreement with literature values<sup>6,40</sup> or are reported in Table 5. <sup>1</sup>H and <sup>13</sup>C NMR, IR and mass spectral studies, as well as elemental analysis, confirmed the stated structures and purity of the products. For the 5-substituted 2,2-dihydroxyindane-1,3-diones, the product is a mixture of two isomers, *i.e.* as shown in Scheme 3. Before recrystallisation as above, the relative compositions were obtained by integrations of <sup>1</sup>H NMR spectra using a JEOL EX270, 270 MHz multinuclear FT instrument and the values of *ratio* shown in Table 2 were found to be reproducible to  $\pm 5\%$ .

## Acknowledgements

We thank Dr A. G. Osborne for his kind and detailed help in the interpretation of NMR spectra.

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Paper 6/06312H  
 Received 13th September 1996  
 Accepted 23rd December 1996