# Reactions of carbonyl compounds in basic solutions. Part 22.[1] The mechanisms of the alkaline hydrolysis of methyl *cis*-3-(substituted benzoyl)-2,3-diphenylacrylates and the 5-methoxy-5-(substituted phenyl)-3,4-diphenylfuran-2(5*H*)-ones, as well as the ionisation of the corresponding acids

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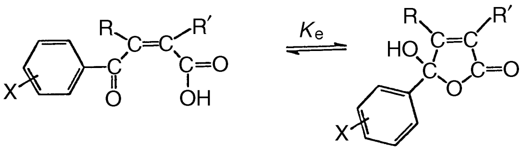
**Rate coefficients have been measured for the alkaline hydrolysis of a series of chain (normal) esters, the methyl *cis*-3-(substituted benzoyl)-2,3-diphenylacrylates, and the corresponding ring (pseudo) esters, the 5-methoxy-5-(substituted phenyl)-3,4-diphenylfuran-2(5*H*)-ones, in 70% (v/v) dioxane–water at 30 °C. Those for the two parent esters were also measured at 45.0 and 60.0 °C and the enthalpies and entropies of activation have been evaluated. A consideration of relative rates, activation parameters and substituent effects indicates hydrolysis of the chain esters with neighbouring group participation by the keto-carbonyl group. The ring esters demonstrate the high reactivity of the five-membered lactone-like system. The steric effects of the phenyl groups does not switch mechanisms, but only modifies reactivity. The equilibrium constants for ring-chain tautomerism in a series of *cis*-3-(substituted benzoyl)-2,3-diphenylacrylic acids have been determined by using the observed p$K_a$ values in 80% (m/m) 2-methoxyethanol–water together with estimated true p$K_a$ (p$K_a^T$) values. The equilibrium constants for these acids have been correlated using the Hammett equation to give $\rho$ as *ca*. 1.3. The results are discussed in terms of steric 'bulk' and resonance effects.**

In a previous study,[2] the alkaline hydrolyses of 3′- and 4′-substituted methyl *cis*-3-benzoylacrylates, **1a**, *cis*-3-benzoyl-3-methylacrylates, **1b**, and *cis*-3-benzoyl-2-methylacrylates, **1c**, were studied. Their reaction mechanism was shown to involve intramolecular catalysis by the neighbouring keto-group. A similar result arose from earlier studies[3,4] of the alkaline hydrolysis of 3′- and 4′-substituted methyl 2-benzoylbenzoates, **2**, and methyl 8-(3- and 4-substituted-benzoyl)-1-naphthoates, **3**. A study[5] of the alkaline hydrolysis of the corresponding ring (pseudo) esters, **4** and **5**, indicated a stepwise mechanism with rate-determining attack of hydroxide anion on the carbonyl group. For the full investigation of the factors controlling reactivity and mechanism in such systems, especially steric 'bulk' effects, a further model has been designed. This model should have a *cis*-ethylenic link, relatively stable chain (normal) and ring (pseudo) methyl esters and 'bulky' flanking substituents at the double bond. Such a system is the chain and ring methyl esters of *cis*-3-benzoyl-2,3-diphenylacrylic acids, **1d** and **6**, respectively.

Ring–chain tautomerism has been shown to occur in a number of *cis*-3-aroylacrylic acids **7a**, **8a**, **7b**, **8b** and **7c**, **8c**,[6] as shown, for example, in eqn. (1). The equilibrium constant, $K_e$, for the tautomeric equilibrium (1) is given by eqn. (2). It is possible to use a number of methods, *e.g.* IR, UV and $^1$H NMR spectroscopy, to make quantitative studies of these equilibria.[7]



(1)

$$K_e = a_{ring}/a_{chain} \qquad (2)$$

However, it is very difficult to use any of these methods if one of the tautomeric forms is highly predominant. If the predominant form is relatively much less acidic than the other, it is possible to use measurement of p$K_a$ values to achieve the measurement of $K_e$. Thus, the true p$K_a$ value, p$K_a^T$, is related to the observed value by the relation (3).[8] If the p$K_a$ is known and a reliable estimate of the p$K_a^T$ can be made, $K_e$ can be calculated.

$$pK_a^T = pK_a - \log (K_e + 1) \qquad (3)$$

Earlier studies[9] had suggested that the chain (normal) *cis*-3-benzoyl-2,3-diphenylacrylic acids, **7d**, are present as the ring (pseudo) 5-hydroxy-3,4,5-triphenylfuran-2(5*H*)-ones, **8d**, mainly from their IR spectra.

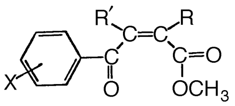
We describe here the alkaline hydrolysis of a series of methyl *cis*-3-(substituted benzoyl)-2,3-diphenylacrylates, the chain (normal) esters, **1d**, and 5-methoxy-5-(substituted phenyl)-3,4-diphenylfuran-2(5*H*)-ones, the ring (pseudo) esters, **6**. The effects of substitution, relative rates and activation parameters are considered in terms of detailed mechanisms and are related to the factors governing reactivity in such systems. The tautomeric equilibrium of a series of *cis*-3-(substituted benzoyl)-2,3-diphenylacrylic acids has been investigated, using IR spectroscopic and ionisation methods. The latter method enabled determination of the $K_e$ values for these acids and the results are discussed in terms of the polar, steric and stereochemical effects present.

## Results

The alkaline hydrolysis of all the methyl esters is of first-order in both ester and hydroxide anion. Rate coefficients for the alkaline hydrolysis of methyl *cis*-3-(substituted benzoyl)-2,3-diphenylacrylates and 5-methoxy-5-(substituted phenyl)-3,4-diphenylfuran-2-(5*H*)-ones at 30.0 °C in 70% (v/v) dioxane–water are shown in Table 1 and, for the parent esters, at 30.0, 45.0 and 60.0 °C in Table 2. The activation parameters for the esters, included in Table 2, are shown in Table 3.

### IR measurements

The carbonyl stretching vibrations of the acids and the chain (normal) and ring (pseudo) methyl esters are shown in Table 4.

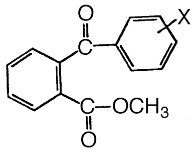


**1a** R = R′ = H

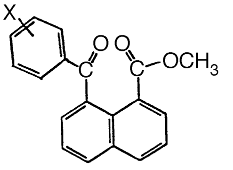
**1b** R = H, R′ = $CH_3$

**1c** R = $CH_3$, R′ = H

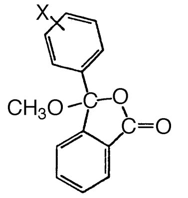
**1d** R = R′ = Ph



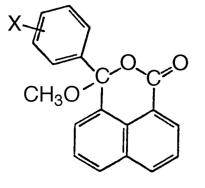
**2**



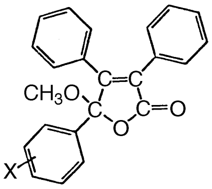
**3**



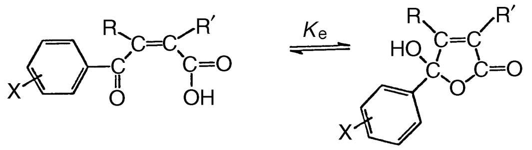
**4**



**5**



**6**



(1)

**7a** R = R′ = H

**b** R = H, R′ = $CH_3$

**c** R = $CH_3$, R′ = H

**d** R = R′ = Ph

**8a** R = R′ = H

**b** R = H, R′ = $CH_3$

**c** R = $CH_3$, R′ = H

**d** R = R′ = Ph

The spectra of all the acids show the presence of the ring tautomer alone. In a most favourable case, 2% of the chain tautomer could have been detected and $K_e$ would then be equal to 49. Thus, this can be considered an upper limiting value for this type of measurement.

### NMR measurements

The $^1H$ NMR spectra were not capable of yielding any useful information regarding tautomeric states, *i.e.* the acid, chain (normal) and ring (pseudo) methyl esters had almost identical aryl $^1H$ NMR spectra. The $^{13}C$ NMR spectra of the chain (normal) methyl esters in $CDCl_3$ had signals at *ca.* 168 ppm (ester carbonyl) and 190 ppm (keto carbonyl), while the ring (pseudo) methyl esters had signals at *ca.* 166 ppm (lactone carbonyl) and 110 ppm (lactol carbon). The spectra of the corresponding acids had signals corresponding to those of the ring (pseudo) esters. However, the nature of the $^{13}C$ NMR spectra made any quantitative conclusions impossible.

**Table 1** Rate coefficients ($k_2$) for the alkaline hydrolysis of methyl *cis*-3-(substituted benzoyl)-2,3-diphenylacrylates and the corresponding 5-methoxy-5-(substituted phenyl)-3,4-diphenylfuran-2(5*H*)-ones in 70% (v/v) dioxane–water at 30.0 °C[a]

| | $k_2$/dm$^3$ mol$^{-1}$ s$^{-1}$ ($\lambda$/nm)[b] | |
|---|---|---|
| Substituent | *cis*-3-Benzoylacrylates | 5-Methoxyfuran-2(5*H*)-ones |
| H | 0.0247 (250) | 0.0333 (250) |
| 4-$CH_3$ | 0.0150 (256) | 0.0227 (260) |
| 4-$OCH_3$ | 0.0120 (295) | 0.0239 (280) |
| 4-Cl | 0.0580 (254) | 0.0596 (260) |
| 3-Cl | 0.0700 (246) | 0.0644 (250) |

[a] Rate coefficients were reproducible to within ±3%. [b] Wavelength used to monitor alkaline hydrolysis.

**Table 2** Rate coefficients ($k_2$) for the alkaline hydrolysis of methyl *cis*-3-benzoyl-2,3-diphenylacrylate and 5-methoxy-3,4,5-triphenylfuran-2(5*H*)-one in 70% (v/v) dioxane–water[a]

| | $k_2$/dm$^3$ mol$^{-1}$ s$^{-1}$ | | |
|---|---|---|---|
| | at 30.0 °C | at 45.0 °C | at 60.0 °C |
| Methyl *cis*-3-benzoyl-2,3-diphenylacrylate | 0.0247 | 0.733 | 0.212 |
| 5-Methoxy-3,4,5-triphenylfuran-2(5*H*)-one | 0.0333 | 0.946 | 0.251 |

[a] See Table 1.

**Table 3** Activation parameters for the alkaline hydrolysis of methyl *cis*-3-benzoyl-2,3-diphenylacrylate and 5-methoxy-3,4,5-triphenylfuran-2(5*H*)-one in 70% (v/v) dioxane–water at 30.0 °C[a]

| | $\Delta H^‡$/kcal mol$^{-1}$ [b] | $\Delta S^‡$/cal mol$^{-1}$ K$^{-1}$ [b] |
|---|---|---|
| Methyl *cis*-3-benzoyl-2,3-diphenylacrylate | 13.8 (±0.3) | −20 (±1) |
| 5-Methoxy-3,4,5-triphenylfuran-2(5*H*)-one | 12.9 (±0.3) | −23 (±1) |

[a] Uncertainties shown in parentheses. [b] 1 cal = 4.184 J.

**Table 4** Carbonyl stretching frequencies of *cis*-3-(substituted benzoyl)-2,3-diphenylacrylic acids and the corresponding chain (normal) and ring (pseudo) methyl esters in $CHCl_3$

| | $\nu_{max}$/cm$^{-1}$ | | |
|---|---|---|---|
| Substituent | Acid | Normal ester | Pseudo ester |
| H | 1765 | 1670, 1719 | 1768 |
| 4-$CH_3$ | 1764 | 1671, 1719 | 1768 |
| 4-$OCH_3$ | 1761 | 1669, 1718 | 1766 |
| 4-Cl | 1766 | 1672, 1720 | 1769 |
| 3-Cl | 1767 | 1674, 1721 | 1770 |

### p$K_a$ measurements

The apparent p$K_a$ values of the acids in 80% (m/m) 2-methoxyethanol (MCS)–water at 25 (± 0.1) °C are shown in Table 5.

## Discussion

### Alkaline hydrolysis of the chain (normal) esters

The occurrence of intramolecular catalysis by keto groups in the alkaline hydrolysis of esters has been detected by the use of three main criteria, *i.e.* relative rates, activation parameters and reaction constants.[10]

An estimate of the ‘normal’ rate of the alkaline hydrolysis of methyl *cis*-3-benzoyl-2,3-diphenylacrylate can be made by using the known steric and polar effects of *cis*-3-substituents on the alkaline hydrolysis of methyl acrylate.[11] The rate ratio of methyl *cis*-3-benzoyl-2,3-diphenylacrylate relative to that of methyl *trans*-2,3-diphenylacrylate ($k_2$ at 30.0 °C equal to 0.0403 dm$^3$

**Table 5** Ionization of and equilibrium constants ($K_e$) for ring-chain tautomerism of the *cis*-3-(substituted benzoyl)-2,3-diphenylacrylic acids in 80% (m/m) 2-methoxyethanol–water at 25 °C[a]

| Substituent | Observed p$K_a$ | Estimated p$K_a^T$ | $10^{-2}K_e$ |
|---|---|---|---|
| H | 9.37 | 6.17 | 16 (±4) |
| 4-$CH_3$ | 9.27 | 6.27 | 10 (±3) |
| 4-$OCH_3$ | 8.87 | 6.24 | 4 (±1) |
| 4-Cl | 9.34 | 6.05 | 20 (±5) |
| 3-Cl | 9.60 | 5.99 | 41(±11) |

[a] The observed p$K_a$ values were reproducible to ±0.03 unit. Those estimated are considered to be reliable to ±0.07 unit.

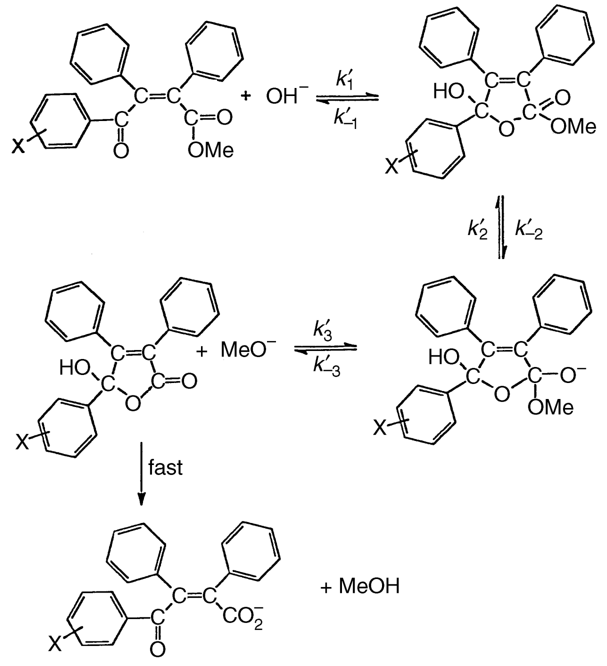
mol$^{-1}$ s$^{-1}$)[12] is equal to 6.1; whereas that expected for 'normal' hydrolysis is *ca.* 1.0, *cf.* ref. 2. Thus, the enhanced rate ratio is *ca.* 6. This small enhancement is only indicative, not demanding, of intramolecular catalysis. A direct comparison of the rate of alkaline hydrolysis of the ester studied here with those for methyl *cis*-3-benzoylacrylate and *cis*-3-benzoyl-3-methylacrylate[2] shows that the 2- and 3-phenyl groups strongly inhibit the reaction, *i.e.* give a rate decrease by a factor of *ca.* 0.08. This is presumably due to the steric 'bulk' effect of the phenyl groups.[13] However, this would occur whether hydroxide anion attack was at the benzoyl or ester group.

The activation parameters previously found for the alkaline hydrolysis of methyl *cis*-3-benzoylacrylate and *cis*-3-benzoyl-3-methylacrylates were very distinctive with very small enthalpies of activation and large negative entropies of activation.[2] However, those found in the present study for the *cis*-3-benzoyl-2,3-diphenylacrylate system, shown in Table 3, are in the range of those usually found for both the 'normal' alkaline hydrolysis of esters and related systems and some less reactive esters employing intramolecular hydrolysis.[10] Again an increased enthalpy of activation would be expected to arise from the 'bulk' steric effect of the 2,3-diphenyl groups.[13]

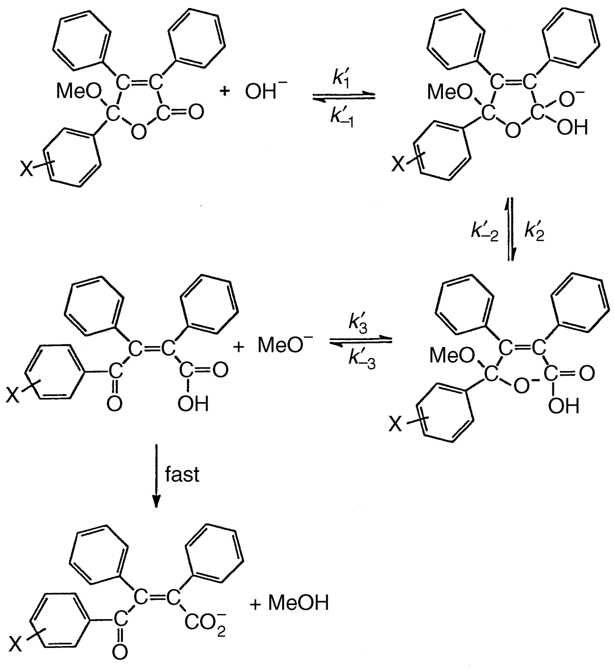
The effect of substitution in the phenyl ring in the benzoyl esters, **1d**, was assessed using the Hammett eqn. (4) below. The

$$\log (k/k_0) = \rho\sigma \qquad (4)$$

reaction constant, $\rho$, found for substitution in the 3-benzoyl group is *ca.* 1.23 (see Table 6). The value of $\rho$ for the alkaline hydrolysis of methyl benzoates under identical conditions is 2.20.[3] The latter can be taken as the reference reaction, $\rho_0$. Then, the reaction constant ratio, $\rho/\rho_0$, expected for 'normal' unassisted hydrolysis can be calculated to be *ca.* 0.3, based on simple transmissive factors.[14] Furthermore, the ratio found for the hydrolysis of the methyl *trans*-3-benzoylacrylate systems is 0.32.[2] However, for the alkaline hydrolysis of methyl *cis*-3-benzoylacrylate and *cis*-3-benzoyl-3-methylacrylates, $\rho/\rho_0$ values of about $1.0_5$ and $0.8_5$, respectively, were found.[2] This is very strong evidence for the occurrence of intramolecular catalysis. The value of $\rho/\rho_0$ equal to *ca.* $0.5_5$ found in the present study clearly indicates that intramolecular catalysis is occurring and that negative charge is commencing transfer to the ester carbonyl oxygen as the intramolecular attack proceeds. The mechanistic pathway would appear to be that shown in Scheme 1. The rate-determining step is suggested to be $k'_2$ on the basis of the reaction constant observed.



**Scheme 1**



**Scheme 2**

## Alkaline hydrolysis of the ring (pseudo) esters

A direct comparison of the present reaction system can be made with our previous study[5] of alkaline hydrolysis of the ring (pseudo) methyl 8-(substituted benzoyl)-1-naphthoates (six-membered ring) and 2-(substituted benzoyl)benzoates (five-membered ring). The mechanistic pathway suggested is shown in Scheme 2. The rate-determining step is considered to be $k'_1$, with a relatively rapid ring fission. The ring strain in such systems is released in the step $k'_2$, *cf.* ref. 5. The relatively greater reactivity of these ring esters, compared to chain esters undergoing 'normal' or unassisted hydrolysis, arises from the *cis* conformation of the ester group as has been noted for simple, up to seven-membered ring, lactones.[15,16] The rate of hydrolysis for the diphenyl system is *ca.* 0.13 that of the ring (pseudo) methyl 2-benzoylbenzoate at 30 °C, both of which are five-membered rings. This decrease in reactivity again apparently arises from the steric 'bulk' effect of the phenyl groups retarding attack of the carbonyl group. The activation parameters for both these five-membered systems are very comparable. The Hammett reaction constant, $\rho$, found for these ring esters of *ca.* 0.78, as shown in Table 6, is almost the same as that found for the five-membered ring methyl esters of 2-benzoylbenzoic acids,[5] when corrected to 30 °C, *i.e.* 0.79. The reaction constant ratio, $\rho/\rho_0$, for the diphenyl system, equal to *ca.* $0.3_5$, agrees with the value of *ca.* 0.3, based on simple transmissive factors,[14] calculated for the formation of the tetrahedral intermediate from the ring ester and hydroxide anion, *i.e.* $k'_1$ (Scheme 2).

**Table 6** Hammett reaction constants ($\rho$) for the alkaline hydrolysis of the methyl esters in 70% (v/v) dioxane–water at 30.0 °C and for the ionization and ring-chain tautomerism of the *cis*-3-(substituted benzoyl)-2,3-diphenylacrylic acids in 80% MCS–water at 25 °C [a]

| System | $\rho$ | $\log k_0$ | $r$ | $s$ | $n$ |
|---|---|---|---|---|---|
| Alkaline hydrolysis of methyl *cis*-3-(3- or 4-substituted benzoyl)-2,3-diphenylacrylates | 1.23 | −1.60 | 0.999 | 0.03 | 5 |
| Alkaline hydrolysis of 5-methoxy-5-(3- or 4-substituted-phenyl)-3,4-diphenylfuran-2(5*H*)-ones | 0.78 | −1.46 | 0.967 | 0.10 | 5 |
| Ionization of acids (observed p$K_a$) | −0.82 | $-9.26_5$ | 0.843 | 0.30 | 5 |
| Ring-chain tautomerism of acids ($K_e$) | 1.30 | $3.09_5$ | 0.948 | 0.25 | 5 |
| As above | 1.04 ($\rho_I$), 1.66 ($\rho_R$) | 3.23 | 0.999 | 0.07,[b] 0.09[c] | 5 |

[a] $r$ is the correlation coefficient, $s$ the standard deviation and $n$ the number of substituents used. [b] Relates to $\rho_I$. [c] Relates to $\rho_R$.

The reactivity–selectivity principle[17] has not been found to apply to the alkaline hydrolysis of a comprehensive series of substituted phenyl ring (pseudo) esters of formyl and keto-carboxylic acids.[18] This is also true for the ring (pseudo) methyl esters of substituted benzoyl carboxylic acids studied here. Thus, for the alkaline hydrolysis of the ring esters, the order of reactivity at 30 °C is: 2-benzoylbenzoates > 8-benzoyl-1-naphthoates > *cis*-3-benzoyl-2,3-diphenylacrylates; while the selectivity at, or corrected to, 30 °C is: *cis*-3-benzoyl-2,3-diphenylacrylates ≈ 2-benzoylbenzoates > 8-benzoyl-1- naphthoates.

Both the series of methyl chain (normal) and ring (pseudo) *cis*-3-benzoyl-2,3-diphenylacrylates are more reactive in alkaline hydrolysis than the corresponding simple esters. The chain esters hydrolyse by employing neighbouring group participation by the keto-carbonyl group; while the increased reactivity of the ring esters is derived from their *cis* conformation, arising from the constraints of ring formation. The significant steric 'bulk' effects of the two phenyl groups (one buttressing the other) are not sufficient to give rise to any mechanistic switches.

### Ionisation and ring-chain tautomerism

While both the IR and NMR spectral evidence indicates that the acids are predominately in the ring (pseudo) form, the ionization studies allow a quantitative analysis of ring–chain tautomerism in this system. The acidity of a substituted carboxylic acid is very much greater than that of a hemi-ketal, *i.e. ca.* 7 p$K_a$ units.[19] Reliable acidity measurements have been made in 80% MCS–water for a number of different Brønsted acids, which can be related to measurements in water. The hemi-ketal can be expected to have a p$K_a$ in 80% MCS–water of *ca.* 13.5, *cf.* ref. 20. Thus, the ionization measurements made in this study refer to the ionization of the chain (normal) carboxylic acid modified by the occurrence of ring-chain tautomerism, as expressed in eqn. (3). The p$K_a^T$ values for these acids can be reliably estimated from the known p$K_a$ values, under identical conditions, for the *cis*-3-(substituted benzoyl)acrylic acids,[6,21] **7a** and for *trans*-α-phenylcinnamic and acrylic acids.[21,22] Thus, simple additivity of substituent effects on the p$K_a$ values of acids in 80% MCS–water has been demonstrated.[19] Early studies[23] indicated that the *cis*-3-benzoylacrylic acids were predominantly present as the chain tautomer and a previous study[21] estimated $K_e$ for the parent acid of this series to be 0.3 (±0.2). In Table 5 are shown the estimated p$K_a^T$ values and the values of $K_e$ derived by use of eqn. (3), for the *cis*-3-(substituted benzoyl)-2,3-diphenylacrylic acids.

First, the value of $K_e$ for the parent *cis*-3-benzoyl-2,3-diphenylacrylic acid, **7d** *i.e.* 1600, is dramatically increased compared to those for *cis*-3-benzoylacrylic acid, **7a**, the 2-methyl, **7b**, and 3-methyl, **7c**, acids, *i.e.* 0.3, 7 and 11, respectively.[6] This increase must result from two sources. The first is a severe decrease in steric crowding and 'bulk' interactions present in the ring tautomer, compared to those present in the chain tautomer. The second is the increase in resonance interactions in the *cis*-stilbene structure in the chain tautomer as decreased steric interactions allow reduced twisting of the 2,3-diphenyl groups out of coplanarity with the ethylenic link. Crowded systems appear, in general, to favour the ring tautomer in keto-carboxylic acids, particularly when the latter tautomer occurs as a five-membered furan-2(5*H*)-one.

Secondly, the effect of substitution on the reactivity in this system can be assessed using the Hammett equation (4). The correlations are shown in Table 6. The very poor correlations given for the observed p$K_a$ values are not unexpected. Previously, it has been shown[24] that, if $1 \ll K_e$, as in this study, the $\rho$ derived from the observed p$K_a$ values will approximate to the sum of the reaction constants for p$K_a^T$ and for $\log K_e$. Such a correlation can be expected to be poor due to the combination of the inexact nature of two such correlations. As such the correlation is not valid for such systems. However, the correlation of $\log K_e$ with $\sigma$ is reasonably satisfactory, as shown in Table 6, and gives the expected positive $\rho$ value, *cf.* refs. 6, 24, 25. The modified Hammett equation (5), shown, can be used to

$$\log (K/K_0) = \rho_I\sigma_I + \rho_R\sigma_R{}^0 \qquad (5)$$

give a somewhat improved correlation, using $\sigma_I$ and $\sigma_R{}^0$,[26] as shown in Table 6. This equation has been previously employed with success in the correlation of $K_e$ values for substituted *cis*-3-benzoyl-3-methylacrylic, *cis*-3-benzoylacrylic and 8-benzoyl-1-naphthoic acids.[6,25] As in the latter studies,[6,25] the greater importance of resonance effects, as indicated by $\rho_R$, than 'inductive' effects, as indicated by $\rho_I$, is demonstrated. This results from the stabilisation of the chain tautomer by electron-releasing resonance effects between the substituent and the keto-carbonyl group and *vice versa*.

## Experimental

### Materials

The acids were prepared by reaction of the appropriate arylcadmium with diphenylmaleic anhydride, using the method of Weinberg and Miller.[27] The chain (normal) methyl esters, **1d**, were prepared from the corresponding acids by the reaction of the appropriate acid with diazomethane in diethyl ether. The corresponding ring (pseudo) methyl esters, **6**, were prepared by the method of Rio and Hardy[23] in two stages; *i.e.* the cyclic acid chloride was prepared from the appropriate acid by treatment with thionyl chloride, followed by solvolysis of the chloride in methanol. The purity of the acids and methyl esters was monitored by $^1$H and $^{13}$C NMR spectroscopy, as well as by IR spectroscopy. The chemical shifts of the methyl group of the chain (normal) esters, **1d**, were observed in $CDCl_3$ at 3.59–3.61 ppm and those of the ring (pseudo) esters, **6**, at 3.51–3.54 ppm. The mp values of the acids and esters, after repeated recrystallization and drying under reduced pressure ($P_2O_5$), were in agreement with literature values[27] or are shown in Table 7, together with the elemental analysis.

The solvents were purified as described previously.[3,24,28]

### Kinetic measurements

Rate coefficients for the alkaline hydrolysis of the esters were determined spectrophotometrically by use of a Perkin-Elmer Lambda 5 UV–VIS spectrometer. The reactions were followed

**Table 7** Physical constants of previously unreported acids and methyl esters

| | | Found (%) (required) | | |
|---|---|---|---|---|
| Acid, **7d**/**8d** (formula) | Mp/°C[a] | C | H | Cl |
| 4-$CH_3$($C_{23}H_{18}O_2$) | 179–180 | 80.9 | 5.2 | |
| | | (80.7) | ($5.2_5$) | |
| 4-$OCH_3$($C_{23}H_{18}O_3$) | 142–143 | 76.9 | 5.1 | |
| | | (77.1) | ($5.0_5$) | |
| 3-Cl($C_{22}H_{15}ClO_3$) | 156–157 | 72.7 | 4.1 | $9.7_5$ |
| | | (72.8) | ($4.1_5$) | (9.8) |
| | | Found (%) (required) | | |
| Chain methyl ester, **1d** (formula) | | C | H | Cl |
| 4-$CH_3$($C_{24}H_{20}O_3$) | 127–128 | 81.0 | 5.6 | |
| | | (80.9) | (5.6) | |
| 4-$OCH_3$($C_{24}H_{20}O_4$) | 164–165 | 77.2 | 5.4 | |
| | | (77.4) | (5.4) | |
| 4-Cl($C_{23}H_{17}$ $ClO_3$) | 122–123 | 73.2 | 4.5 | 9.4 |
| | | (73.3) | (4.5) | (9.4) |
| 3-Cl($C_{23}H_{17}ClO_3$) | 93–94 | 72.9 | 4.5 | 9.4 |
| | | (73.3) | (4.5) | (9.4) |
| Ring methyl ester, **6** (formula) | | | | |
| 4-$CH_3$($C_{24}H_{20}O_3$) | 102–103 | 80.7 | 5.6 | |
| | | (80.9) | (5.6) | |
| 4-$OCH_3$($C_{24}H_{20}O_4$) | 121–122 | 77.2 | 5.4 | |
| | | (77.4) | (5.4) | |
| 4-Cl($C_{23}H_{17}ClO_3$) | 112–113 | 73.2 | 4.5 | $9.3_5$ |
| | | (73.3) | (4.5) | (9.4) |
| 3-Cl($C_{23}H_{17}ClO_3$) | 118–119 | 73.3 | 4.5 | 9.4 |
| | | (73.3) | (4.5) | (9.4) |

[a] Recrystallised from benzene–hexane (**7d/8d**), methanol (**1d**) or cyclohexane (**6**).

at the wavelengths shown in Table 1. The procedure used was that described previously.[4] The products of the reactions were found to be the anions of the corresponding acids in quantitative yield in all cases and were further confirmed spectrophotometrically by comparison of the spectrum of the acid in base with that of the reaction product.

### IR measurements

The carbonyl stretching vibrations of the acids and their chain and ring methyl esters were determined as previously described[6,28] for solutions (0.02 mol $dm^{-3}$) in $CHCl_3$ at 35 (±1) °C. A Perkin-Elmer model 1600 FTIR spectrophotometer was used in these studies and the wavenumber measurements were reproducible to ±1 $cm^{-1}$.

### NMR measurements

The spectra of the compounds were measured using a JEOL EX270 spectrometer operating at 270 MHz. The $^1H$ NMR spectral chemical shifts were measured in ppm relative to $SiMe_4$ and the $^{13}C$ NMR spectral chemical shifts in ppm relative to $SiMe_4$.

### p$K_a$ measurements

The apparent p$K_a$ values of the acids in 80% (m/m) 2-methoxyethanol (MCS)–water at 25 (±0.1) °C were measured as described previously.[3] All the determinations are the results of at least two separate determinations.

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