Reactions of carbonyl compounds in basic solutions. Part 25.[1] The mechanism of the base-catalysed ring fission of 3,4-diphenylcyclobut-3-ene-1,2-diones

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The rate coefficients for the base-catalysed ring fission of a series of substituted 3,4-diphenylcyclobut-3-ene-1,2-diones to give the corresponding (Z)-2-oxo-3,4-diphenylbut-3-enoic acids have been determined in 50% (v/v) aqueous dimethyl sulfoxide (DMSO) at 25.0 and 45.0 °C, as well as for a limited series in 70% (v/v) aqueous DMSO. The activation parameters have been calculated. The effect of both mono- and di-substitution of the phenyl groups has been studied and gives a Hammett ρ value of *ca.* 1.3 in 50% aqueous DMSO at 25.0 °C. The kinetic solvent isotope and solvent effect and enrichment in ^{18}O-enriched water have been studied. The product composition of the reaction of the monosubstituted compounds gave a ρ value of *ca.* 0.9. All the evidence indicates a mechanistic pathway which proceeds by a rapid, reversible addition of hydroxide anion to the dione, followed by a benzilic acid-type rearrangement to form a 1-hydroxycyclopropene-1-carboxylic acid. The latter then suffers ring fission to give the final product.
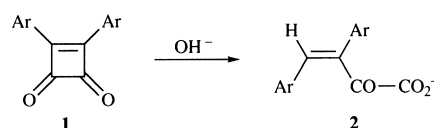
The base-catalysed ring fission of cyclobutenediones has been studied by several groups.[2–4] However, no definitive reaction mechanism has been established. Thus, Skattebøl and Roberts[2] suggested that the dione adds hydroxide anion to form the anion of the mono-hydrate, which collapses to give a 1-hydroxy-cyclopropene-1-carboxylic acid anion. The latter suffers ring fission to give a 2-oxobut-3-enoic acid as the immediate reaction product. However, Blomquist and LaLancette[3] indicated a pathway involving addition of water to the activated ethylenic bond, catalysed by hydroxide anion, followed by addition of hydroxide anion to carbonyl group β to the hydroxy substituent. Thus, these cyclobutenediones react by bond fission of the carbonyl carbon–olefinic carbon. On the contrary, the base-catalysed ring fission of benzocyclobutenediones results in the formation of 2-formylbenzoic acids, which involves fission of the carbonyl carbon–carbonyl carbon bond in the cyclobutene-dione ring.[1] However, a benzilic acid-type of rearrangement has been demonstrated in the base-catalysed reactions of cyclo-butanediones to form 1-hydroxycyclopropane-1-carboxylic acids.[5] An important study by DeBoer[6] has shown that, when ethyl 3-hydroxy-1,2-diphenylcyclopropene-3-carboxylate† was

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† More correct name: ethyl 1-hydroxy-3,4-diphenylcyclopropene-1-carboxylate. IUPAC preferred names have been used throughout this paper.

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treated with sodium methoxide in methanol or a catalytic amount of 1,5-diazabicyclo[4.3.0]non-5-ene in chloroform or benzene, a quantitative reverse benzilic acid-type rearrangement gives 1,2-diphenylcyclobutene-3,4-dione. The latter ring did not undergo ring cleavage under these mild conditions. This result gives support to the pathway proposed by Skattebøl and Roberts.[2]

We describe here the base-catalysed ring fission of a series of substituted 3,4-diphenylcyclobut-3-ene-1,2-diones **1**. The products and their distribution, the effect of substituents on the rates, activation parameters, solvent and solvent kinetic effects and hydrolysis in ^{18}O-enriched water have been studied. The detailed mechanistic pathway has been elucidated and is discussed in relation to related reactions.

Results

The base-catalysed ring fission of the substituted 3,4-diphenyl-cyclobut-3-ene-1,2-diones **1** gives the corresponding (Z)-2-oxo-3,4-diphenylbut-3-enoates **2** in quantitative yield. The reaction

Table 1 Rate coefficients (k_2) and product ratios (*Ratio*) for the base-catalysed ring fission of substituted 3,4-diphenylcyclobut-3-ene-1,2-diones in aqueous DMSO ($\mu = 0.1$ mol dm^{-3})[a]

| Substituent(s)[b] | | k_2/dm^3 mol^{-1} s^{-1} | | | | | |
| | | in 50% (v/v) aqueous DMSO | | in 70% (v/v) aqueous DMSO | | | |
X	Y	at 25.0 °C	at 45.0 °C	at 25.0 °C	at 45.0 °C	*Ratio*	λ/nm[c]
H	H	70.7	117	311	363	1.0	269
CH$_3$	H	40.6	74.0	178	229	0.75 ($\pm$0.06)	274
OCH$_3$	H	22.0	40.6	88.8	129	0.67 ($\pm$0.06)	282
Cl	H	123	190			1.5 ($\pm$0.1$_5$)	274
Br	H	128	211			1.6$_5$ ($\pm$0.1$_5$)	276
CH$_3$	CH$_3$	24.7	47.9	106	152		280
OCH$_3$	OCH$_3$	11.0	22.4	36.9	61.0		306
Cl	Cl	212	339				280
Br	Br	235	373				283

[a] Rate coefficients were reproducible to $\pm$3%. [b] Substituent X is at the 4-position of one phenyl ring (shown as Ar in diagrams) and substituent Y at the 4-position of the other. [c] Wavelength used to monitor the reaction.

Table 2 Activation parameters for the base-catalysed ring fission of substituted 3,4-diphenylcyclobut-3-ene-1,2-diones in aqueous DMSO ($\mu = 0.1$ mol dm^{-3}) at 30 °C [a]

Substituent(s) [b]		in 50% (v/v) aqueous DMSO		in 70% (v/v) aqueous DMSO	
X	Y	$\Delta H^{\ddagger}$/kcal mol^{-1}	$\Delta S^{\ddagger}$/cal mol^{-1} K^{-1}	$\Delta H^{\ddagger}$/kcal mol^{-1}	$\Delta S^{\ddagger}$/cal mol^{-1} K^{-1}
H	H	4.1_5 (8.2) [c]	-36 (-26) [c]	0.8_5	-44
CH$_3$	H	5.1	-34	1.7_5	-42
OCH$_3$	H	5.2	-35	2.9	-40
Cl	H	3.5	-37		
Br	H	4.1	-35		
CH$_3$	CH$_3$	5.6	-33	2.8	-40
OCH$_3$	OCH$_3$	6.1	-33	4.1_5	-37
Cl	Cl	3.8	-35		
Br	Br	3.7_5	-35		

[a] Values of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ are considered accurate to within ± 300 cal mol^{-1} and ± 2 cal mol^{-1} K^{-1}, respectively (1 cal = 4.184 J). [b] See footnote b in Table 1. [c] In water containing 0.33% (v/v) DMSO.

Table 3 Rate coefficients (k_2) for the base-catalysed ring fission of 3,4-diphenylcyclobut-3-ene-1,2-dione in aqueous DMSO and dioxane ($\mu = 0.1$ mol dm^{-3}) at 25.0 °C [a]

Volume (%) non-aqueous solvent	k_2/dm^3 mol^{-1} s^{-1}	
	DMSO	Dioxane
0 [b]	15.1 (18.3) [c]	15.1 (72.0) [d]
30	28.7	11.9
50	70.7	8.64
60	115	8.13
70	311	7.60

[a,b] See Table 1. [c] In deuterium oxide containing 0.33% (v/v) DMSO. [d] At 60.0 °C.

is of first order in both the diones and hydroxide anion. Rate coefficients for the base-catalysed ring fission of the substituted 3,4-diphenylcyclobut-3-ene-1,2-diones **1** in 50% (v/v) aqueous dimethyl sulfoxide (DMSO) at 25.0 and 45.0 °C are shown in Table 1, as well as those for the five least reactive substrates in 70% (v/v) aqueous DMSO using a UV–VIS spectrophotometric method. The activation parameters for the reactions of these compounds are shown in Table 2. The effects of increasing concentrations of DMSO and dioxane on the rate of ring fission of the parent dione are shown in Table 3, as well as the rate coefficients in both water and deuterium oxide. The rates of reaction are relatively fast and k_2 for parent dione at 25 °C in water is 15.1 dm^3 mol^{-1} s^{-1}, but the rate is only *ca.* 0.05 of that of the ring fission of benzocyclobutene-1,2-dione under the same conditions.[1] The isolated products of ring fission are the substituted (*Z*)-2-oxo-3,4-diphenylbut-3-enoic acids **3**. For the

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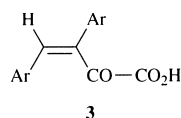
unsubstituted and symmetrically disubstituted diones, only one product was isolated, as expected. However, for the monosubstituted diones **4**, the product can be either the (*Z*)-2-oxo-3-(substituted phenyl)-4-phenylbut-3-enoic acid **5a** or the (*Z*)-2-oxo-3-phenyl-4-(substituted phenyl)but-3-enoic acid **5b**, as shown in Scheme 1. The ratio of 4- to 3-(substituted phenyl) products are given in Table 1 as *Ratio*.
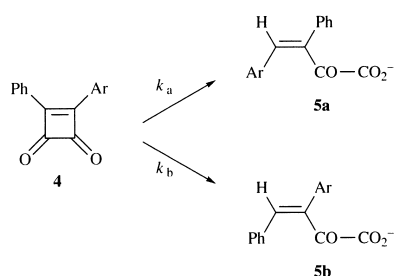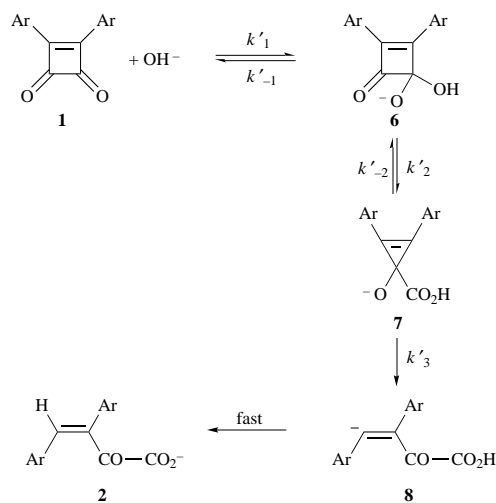

Scheme 1

When the base-catalysed ring fission was studied in ^{18}O-enriched water, the product of ring fission **3** showed three-enrichments; whereas the exchange of the latter acid itself studied under identical base-catalysed conditions gave only one-enrichment.

Discussion

The likely mechanism for the base-catalysed ring fission is shown in Scheme 2. The tetrahedral adduct **6** is initially formed

Scheme 2

in a relatively fast pre-equilibrium. This is confirmed by the study of the hydrolysis in ^{18}O-enriched water which indicates rapid, reversible hydration with equilibration of the adduct. Similar behaviour is shown in the base-catalysed ring fission of benzocyclobutene-1,2-dione[1] and for benzil in the benzilic acid rearrangement.[7] The solvent kinetic isotope effect, $k_2^{D_2O}/k_2^{H_2O}$, was found to be 1.2_1 at 25 °C, as shown in Table 3. This is also in accord with the formation of the adduct in a rapid pre-equilibrium, as also found for the base-catalysed ring fission of benzocyclobutene-1,2-dione[1] and benzilic acid rearrangement.[8] The adduct **6** then collapses to form the anion of 1-hydroxy-3,4-diphenylcyclopropene-1-carboxylic acid **7** in a benzilic acid-type rearrangement.[9] Unlike the ethyl ester of the latter under other conditions,[6] in excess aqueous base, the anion (or dianion) **7** then undergoes ring fission. This could possibly be *via* the carbanion **8**. However, this fission step could appear likely to be concerted with proton transfer to the backside of an orbital that is involved in the carbon–carbon bond that is undergoing cleavage.[10] Thus this reaction involves inversion of configuration at the alkene ring carbon **2**. Recent theoretical treatments of benzilic acid and related rearrangements have indicated alternative paths with similar energetics.[11]

Table 4 Hammett reaction constants (ρ) for the base-catalysed ring fission of the substituted 3,4-diphenylcyclobutene-1,2-diones in 30% aqueous DMSO ($\mu = 0.1$ mol dm^{-3}) at 25 °C [a]

	ρ	$\log k_o$	r	s	n
Mono-substituents with σ_p	1.414	1.794	0.986	0.139	5
Di-substituents with $2\sigma_p$	1.269	1.786	0.996	0.066	5
Mono- and di-substituents with σ_p and $2\sigma_p$	1.298	1.783	0.994	0.056	9
Log ratio with σ_p	0.871	0.035	0.987	0.081	5

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

Activation parameters

The activation parameters for the base-catalysed ring fission of **1** are shown in Table 2. They clearly indicate a bimolecular pathway. In general, electron-withdrawing groups decrease and electron-releasing increase $\Delta H^{\ddagger}$. The values of $\Delta S^{\ddagger}$ do not show any significant variation in 50% aqueous DMSO. However, as the solvent is changed from water to have an increased DMSO content, $\Delta H^{\ddagger}$ values decrease markedly; while $\Delta S^{\ddagger}$ values become somewhat more negative, as has been noted for the alkaline hydrolysis of alkyl benzoates [12] (see also later).

Kinetic substituent effects

The Hammett equation (1) is usually employed in the quantitative assessment of *metal/para*-substituent effects in aromatic

$$\log(k/k_o) = \rho\sigma \quad (1)$$

systems.[13] The rates of the mono- and di-substituted diones have been very successfully correlated separately with σ_p and $2\sigma_p$, respectively, as shown in Table 4. The two ρ values are, within the uncertainties, identical and the two series can be combined to give a ρ value of *ca.* 1.3, using σ_p and $2\sigma_p$ for the mono- and di-substituted series, respectively. Treatments attempting allowance for statistical factors, *i.e.* two identical carbonyl groups in the disubstituted series, do not give improved correlations. There are two important conclusions that can be made from this study of substituent effects. First, the equality of the effect of the first and second identical substitution clearly indicates that the transition state must have a structure in which both substituted phenyl groups are equivalent, *e.g.* close to **7**. Secondly, the observed ρ value of 1.3 in 30% aqueous DMSO at 25 °C can be compared to those for the equilibrium addition of hydroxide anions to benzaldehydes in water at 25 °C (2.2 or 2.8) [14] and the alkaline hydrolysis of ethyl benzoates in water and 65% aqueous DMSO at 25 °C (1.33 and 2.40).[15] These comparisons would indicate that the negative charge developed in the transition state for the present system appears to reside one further 'carbon atom' away,[16] *cf.* the transmission coefficient for C_{sp^2} which equals 0.67.[17] This result would also indicate a transition state structure close to **7** in structure.

Product substituent effects

For the mono-substituted diones **4**, there are two possible products, as shown in Scheme 1, *i.e.* the 4-(substituted phenyl) or 3-(substituted phenyl) carboxylates, **5a** and **5b**, respectively. Using the Wegscheider's principle [18] for concurrent reactions of the same order, Exner [19] has related the amount of both products to the rate coefficients, k_a and k_b, and hence to the reaction constants, ρ_a and ρ_b, for the relevant process in Scheme 1, as shown in eqn. (2), *cf.* ref. 20. As shown in Scheme 2, the product

$$\log(x_a/x_b) = (\rho_a - \rho_b)\sigma \quad (2)$$

determining step is k'_3. The mono-substituent will affect both reaction constants, but the effect on ρ_b is transmitted *via* a further 'carbon atom'. Using the transmission coefficient for C_{sp^2} equal to 0.67,[17] ρ_b can be estimated to be 0.67 ρ_a. Thus, the observed ρ for the product ratio, *Ratio*, equals 0.33 ρ_a. The cor-

relation of log *Ratio* with σ_p is very successful, as shown in Table 4. The ρ value found equals 0.87 and compares closely with the result found by Bird and Harmer [21] for the base-catalysed ring fission of mono-substituted 2,3-diphenylcyclopropenones in methanol at room temperature with ρ equal to 0.75. Thus, ρ_a can be estimated for the present study as *ca.* 2.6. This value suggests that the carbanionic character of the alkene carbon undergoing fission is partially developed, *cf.* ρ for the detritiation of benzyl cyanides in methanol catalysed by methoxide at 25 °C equals 3.9.[22] The effects of substituents cannot be accommodated by the alternative pathway,[3] which involves addition to the ketovinyl double-bond and fission of a cyclobutane-dione ring.

Solvent effects

The effects of solvent on the rates of base-catalysed ring fission of the parent dione are shown in Table 3. The present results can be compared with the effects of solvent composition on the benzilic acid rearrangement,[20] the alkaline hydrolysis of methyl benzoate [12,13] and base-catalysed ring fission of benzocyclobutene-1,2-dione.[1] The rates of reaction increase markedly with increasing DMSO content which is considered to arise mainly from the increased activity of hydroxide. However, the effect of increasing dioxane content on the rates of the base-catalysed reactions has been found to be comparatively minor, but appears to be discriminating with both increases and decreases in rates observed.[23] The behaviour observed for the ring fission of the dione studied here is similar to that of the alkaline hydrolysis of methyl benzoate [23] and very similar to that of the base-catalysed ring fission of benzocyclobutene-1,2-dione.[1] This result favours the formation of charge-localised intermediates like **6** and **7**.

Mechanistic pathway

The conclusions indicate that the reaction proceeds by the pathway shown in Scheme 2. The rate-determining step appears to be the formation of the cyclopropene intermediate **7**; whereas the product-determining step is the breakdown of the latter. The evidence clearly excludes the alternative addition pathway.[3]

In this study, the formation of a very strained cyclopropene from a strained cyclobutene is apparently favoured by the stereochemistry of the attack by the migrating vinyl group. This is in stark contrast to the benzocyclobutene system in which strain apparently becomes so excessive that the fission type switches from carbonyl carbon–carbonyl carbon to carbonyl carbon–aryl carbon.[1]

Experimental

Materials

A direct route [24–26] was employed for the synthesis of the 3,4-diphenylcyclobutene-1,2-diones. 3,4-Dichlorocyclobutene-1,2-dione (squaryl dichloride) [24,25] was reacted with excess of benzene or a substituted benzene, in the presence of 3 equiv. of aluminium chloride and under a blanket of dry nitrogen to give the symmetrically di-(4-substituted phenyl) compounds.[26] Use of benzene and 1 equiv. of aluminium chloride gave 3-chloro-4-phenylcyclobutene-1,2-dione.[24] Reaction of the latter with a substituted benzene as described above gave the 3-phenyl-4-(substituted phenyl)cyclobutene-1,2-diones. The purity of these compounds was monitored by IR, mass and ^{1}H and ^{13}C NMR spectroscopy, as well as by elemental analysis. Their mps, after repeated recrystallisation and drying under reduced pressure (P_2O_5), were in agreement with lit.[26] values or are reported in Table 5.

Inorganic salts were of analytical grade and were used without further purification. The solvents for the kinetic studies were purified as described previously.[27]

Measurements

Rate coefficients for the base-catalysed ring fission of the sub-

stituted 3,4-diphenylcyclobut-3-ene-1,2-diones were determined spectrophotometrically by use of a Perkin-Elmer lambda 5 UV–VIS spectrometer. A Haake thermostatted water circulating bath was used to control the temperature of the cell to ±0.05 °C. The reactions were followed at the wavelengths shown in Table 1. The procedure was that described previously.[27] Buffers were prepared from AnalaR grade chemicals and distilled water (freshly boiled and cooled under N_2 bubbling). The ionic strength was maintained at 0.1 mol dm^{-3} with sodium chloride. The pH of the buffer solutions was measured with a Pye-Unicam model PW9409 direct reading pH meter with glass combination electrode, calibrated with standard buffers at 25 °C. Buffer solution pH was measured using a thermostatted glass vessel at the reaction temperatures. The pD values were obtained by adding 0.40 to the pH meter readings.[28] Both phosphate and borate buffers were used and no buffer catalysis was observed. Buffer concentrations of up to 0.1 mol dm^{-3} and ratio of 1/10 to 10/1 were used. The conversion of pH' in aqueous DMSO to hydroxide concentrations was confirmed by studying the kinetics of the parent dione in aqueous DMSO containing hydroxide. The pH' values in aqueous DMSO were found linear with pOH. The aqueous DMSO solvent was required due to low solubility of certain diones in aqueous solutions.

Product studies

The products of the base-catalysed ring fission of **1** were found to be **2**. For the parent dione, the product was isolated in quantitative yield and was confirmed spectrophotometrically by comparison of the spectrum of the acid in base with that of the reaction product. The mp and elemental analysis of the product is given in Table 5. ^{1}H and ^{13}C NMR, IR and mass spectra confirmed the structure. In an earlier study,[3] the structure of the product was inferred from isolated products, which had arisen from base-catalysed decomposition of the immediate product. In general, the products of the kinetic runs after ten 'half-lives' were isolated by acidification and extraction with diethyl ether. The extract was either evaporated or treated with diazomethane in diethyl ether. The products were then isolated and examined by ^{1}H and ^{13}C NMR, IR and mass spectral studies. For the mono-substituted diones, the product is a mixture of two isomers, *i.e.* as shown in Scheme 2. The relative compositions were obtained by integrations of ^{1}H NMR spectra of the isolated product using a Jeol EX270, 270 MHz multinuclear FT instrument and the values of ratio are shown in Table 1, together with their uncertainties. The ^{1}H NMR spectra show a vinyl proton(s) at 6.5 to 5.5 ppm in deuterated DMSO. These were used to establish the stereochemistry [29] and estimate the composition.

Hydrolysis using ^{18}O-enriched water

The base-catalysed fission of the parent dione was studied by use of ^{18}O-enriched water (4.5 atom%). The reaction was studied under kinetic conditions of excess base for approximately ten 'half-lives' of the dione. After neutralisation and extraction with diethyl ether, the extracts were treated with diazomethane in diethyl ether. The methyl ester of (*Z*)-2-oxo-3,4-diphenylbut-3-enoic acid was isolated. The same procedure was followed

using the acid product itself as substrate. The mass spectrum of the samples and control (using dione and ordinary water) was recorded on an AEI MS12 spectrometer. The enrichment was calculated from the peak areas due to M^+ and $M^+ + 2$.

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