# REACTIONS OF CARBONYL COMPOUNDS IN BASIC SOLUTIONS. PART 34.+ THE MECHANISM OF THE BASE-CATALYSED RING FISSION OF 2,3-DIPHENYLCYCLOPROP-2-EN-1-ONE

Keith BOWDEN[1,*] and Emma J. BURGESS

*Department of Biological and Chemical Sciences, Central Campus, University of Essex, Wivenhoe Park, Colchester, Essex CO4 3SQ, U.K.; e-mail: [1] keithb@essex.ac.uk*

Received May 28, 1999
Accepted June 18, 1999

*Dedicated to Professor Otto Exner on the occasion of his 75th birthday in recognition of his outstanding contributions to physical organic chemistry and chemometrics, and in thanks for his friendship.*

The rate coefficients for the base-catalysed ring fission of a series of 2-phenyl-3-(2-, 3- or 4-substituted phenyl)cycloprop-2-en-1-ones to give the corresponding (*E*)-2,3-diphenylacrylic acids have been determined in water at 30.0 °C, as well as for the unsubstituted compound at 40.0, 50.0 and 60.0 °C. The effects of *meta*- and *para*-substituents on the rates have been correlated using the Hammett equation to give a reaction constant, ρ, equal to *ca* 1.2 at 30 °C. For the unsubstituted compound, the activation parameters have been calculated and the kinetic solvent isotope effect has been studied. The effects of *ortho*-substituents on the rates appear to be mainly polar, rather than steric, in origin. The evidence indicates a mechanistic pathway which proceeds by addition of hydroxide anion to the ketone, which is rate-determining. The adduct suffers ring fission to give the final product *via* a carbanionic intermediate.

**Key words**: Ketones; Ring fission; Cyclopropenones; Substituent effects; Reaction kinetics.

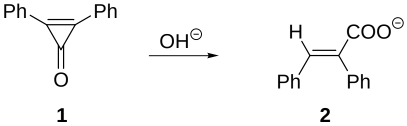
The mechanisms of the base-catalysed ring fission of cyclic 1,2-diones[2,3] and 1,3-diones[4,5] have been studied recently. The pathways and fission-types appear to be related to the ring strain and ring structure present.

2,3-Diphenylcycloprop-2-en-1-one **1** is a strongly polarised ketone and very reactive[6]. With base it is readily cleaved to give the anion of (*E*)-2,3-diphenylacrylic acid[6,7] **2** (Scheme 1). A product study of the base-catalysed fission of a series of 2-phenyl-3-(2-, 3- or 4-substituted phenyl)-

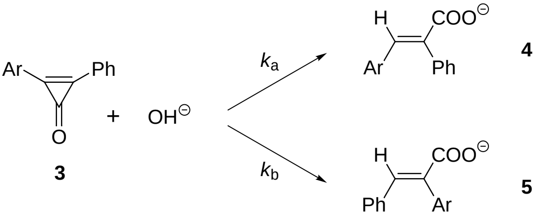
---

+ For Part 33 see ref.[1]

cycloprop-2-en-1-ones **3** has been made by Bird and Hamer[8] which gave a Hammett correlation of the effects of *meta*- and *para*-substituents on the product ratio, log ([**4**]/[**5**]), with a ρ value of *ca* 0.75 and correlation coefficient, *r*, of 0.98 (Scheme 2). The *ortho*-substituents gave predominantly the product **4**, independent of the nature of the *ortho*-substituent. These latter results relate to the product forming steps alone.



SCHEME 1



SCHEME 2

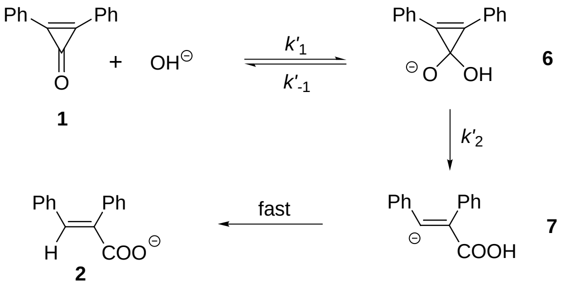
The present report describes a study of the kinetics of the base-catalysed ring fission of 2-phenyl-3-(2-, 3- or 4-substituted phenyl)cycloprop-2-en-1-ones. The effects of substitution and solvent kinetic isotope effect, as well as the activation parameters, have been studied. The detailed mechanistic pathway has been elucidated.

## RESULTS

The base-catalysed ring fission of the substituted 2,3-diphenylcycloprop-2-en-1-ones **3** gives the corresponding substituted (*E*)-2,3-diphenylacrylic acids **4** and **5** in quantitative yield. The reaction is of first order in both the substrate ketones and hydroxide anion. Rate coefficients for the base-catalysed ring fission of the substituted ketones in water at 30.0 °C are shown in Table I, as well as that for the parent ketone in $D_2O$. The rates of reaction are significantly slower than those of the corresponding 3,4-diphenylcyclobut-3-ene-1,2-diones under the same conditions[3] by a factor of *ca* $3 \cdot 10^3$.

## DISCUSSION

The likely mechanism for the base-catalysed ring fission is shown in Scheme 3. The tetrahedral adduct **6** is initially formed. This adduct collapses to form the carbanion **7**, but the fission step could be concerted with proton transfer to the frontside of the orbital that is involved in the carbon–carbon bond that is undergoing cleavage. The latter seems unlikely. Thus the reaction involves retention of the configuration at the alkene ring carbon.



SCHEME 3

TABLE I
Rate coefficients ($k_2$) for the base-catalysed ring fission of substituted 2,3-diphenylcycloprop-2-en-1-ones **3** at 30.0 °C in water[a,b]

| Ar = $C_6H_4X$<br>X | $k_2$, $10^{-3}$ $dm^3$ $mol^{-1}$ $s^{-1}$ | λ, nm[c] |
|---|---|---|
| H | 7.86 (12.4)[d] ($15.2_5$, $28.1_5$, $52.5_5$)[e] | 295 |
| 2'-$CH_3$ | 3.16 | 313 |
| 4'-$CH_3$ | $5.13_5$ | 300 |
| 2'-$OCH_3$ | $3.91_5$ | 282 |
| 3'-$OCH_3$ | 11.5 | 290 |
| 4'-$OCH_3$ | 4.68 | 295 |
| 2'-Cl | $26.5_5$ | 295 |
| 3'-Cl | 26.1 | 295 |
| 4'-Cl | $15.9_5$ | 301 |

[a] Water containing 1.0% (v/v) acetonitrile. [b] Rate coefficients were reproducible to ±3%. [c] Wavelengths used to monitor the reactions. [d] In $D_2O$. [e] At 40.0, 50.0 and 60.0 °C, respectively.

The solvent kinetic isotope effect, $k_2^{D_2O}/k_2^{H_2O}$, was found to be 1.6 at 30 °C, as shown in Table I. This is in accord with the formation of the adduct **6**, and closely similar to those found for the base-catalysis to other related reaction[2–5].

### Activation Parameters

The activation parameters for the base-catalysed fission of the parent substrate **1** are shown in Table II. They clearly indicate a bimolecular pathway. The enthalpy of activation is considerably greater than that of the parent 3,4-diphenylcyclobut-3-ene-1,2-dione in the same reaction[3]. The rate of reaction of the latter is similarly much greater than that of **1**. These both reflect the powerful activating effect of the second strongly electron-withdrawing keto group next to that undergoing reaction in the 1,2-dione.

### Kinetic Substituent Effects

The Hammett equation is usually employed in the quantitative assessment of *meta*/*para*-substituent effects in aromatic systems[9]. The rates of the *meta*- and *para*-substituted ones have been very successfully correlated with σ values, as shown in Eq. (*1*) below.

$$\log k = 1.19\ (\pm 0.08)\sigma - 2.06\ (\pm 0.02) \qquad (1)$$

$$r = 0.991, \qquad n = 6$$

The ρ value found of *ca* 1.2 in water at 30 °C compares closely with that of *ca* 1.3 for the base-catalysed ring fission of the substituted 3,4-diphenyl-

TABLE II
Activation parameters for the base-catalysed ring fission of 2,3-diphenylcycloprop-2-en-1-one in water at 30.0 °C[a]

| | |
|---|---|
| $\Delta H^{\ddagger}$, kcal mol$^{-1}$ | 12.1 (± 0.2) |
| $\Delta S^{\ddagger}$, cal mol$^{-1}$ K$^{-1}$ | –28 (± 1) |

[a] 1 cal = 4.184 J.

cyclobut-3-ene-1,2-diones in 30% aqueous dimethyl sulfoxide at 25 °C. Furthermore, the ρ value for the equilibrium addition of hydroxide anions to benzaldehydes in water at 25 °C is 2.2 or 2.8 (ref.[10]) and for the alkaline hydrolysis of ethyl benzoates in water is 1.33 (ref.[11]). The comparison would indicate that the negative charge in the transition state for the present system appears to reside on the "carbonyl" oxygen, *i.e.* the transition state is close in structure to that of **6**.

The effects of *ortho*-substituents appear to be comparable to those of the *para*-substituents, but somewhat more effective in transmitting their polar effect. In the absence of any steric effect, this is as would be expected for such "*ortho*"-substituents[12], as found for *ortho*-substituted phenylacetic acids[13]. The absence of the "bulk" steric effect for the *ortho*-substituents must arise from the relatively uncrowded nature of the adduct **6**, compared to the substrate **1**.

### *Product Substituent Effects*

For the substituted ketones **3**, there are two possible products **4** and **5**. Using the Wegscheider's principle[14] for concurrent reactions of the same order, Exner[15] has related the amount of both products to the rate coefficients, $k_a$ and $k_b$, and hence to the reaction constants, $\rho_a$ and $\rho_b$, for the relevant process, as shown in Eq. (*2*).

$$\log (x_a/x_b) = (\rho_a - \rho_b)\sigma \tag{2}$$

As shown in Scheme 3, the product determining step is $k'_2$. The substituent will affect both reaction constants, but the effect on $\rho_b$ is transmitted *via* a further "carbon atom". Using the transmission coefficient for $C_{sp^2}$ equal to 0.67 (ref.[16]), $\rho_b$ can be estimated to be 0.67 $\rho_a$. Bird and Harmer[8] found the observed ρ for the product ratio to be 0.75. Thus, $\rho_a$ for this study can be estimated as *ca* 2.3, which suggests that the carbanionic character of the alkene carbon undergoing fission is only partially developed as the ρ value for the detritiation of phenylacetonitrile in methanol catalysed by methoxide at 25 °C equals 3.9 (ref.[17]). These results are very similar to those found for the base-catalysed ring fission of 3,4-diphenylcyclobut-3-ene-1,2-diones[3]. All *ortho*-substituents in the substrate **3** gave the product **4** predominantly and this must arise from a steric "bulk" effect favouring this fission giving a less crowded transition state for **4** than for **5**. However, the stereochemical progress of the present study and that of the dione[3] is quite different. Thus, for the 3,4-diphenylcyclobut-3-ene-1,2-diones, the products involve inversion of configuration at the alkene ring carbon[3]; while, for 2,3-diphenylcycloprop-2-en-1-ones **1**, the product involves retention of configuration[8]. This switch must arise from the difference in the fission leaving groups, *i.e.* $COCO_2H$ and $CO_2H$. Such dependence on the leaving group has been observed previously[18], but not for these particular groups and/or system.

### *Mechanistic Pathway*

The conclusions indicate the reaction proceeds by the pathway shown in Scheme 3, with the rate-determining step being the formation of the adduct **6**. The product determining step is the breakdown of the latter. The adduct **6** suffers less angle strain that the substrate **1** which facilitates reaction compared to comparable alicyclic ketones.

## EXPERIMENTAL

### Materials

The 2-phenyl-3-(2-, 3- or 4-substituted phenyl)cycloprop-2-en-1-ones **3** were prepared by the reaction of the appropriate arylidene chloride with phenylketene dimethylacetal and potassium *tert*-butoxide by Dr C. W. Bird and his co-workers[8,19], as were the corresponding acrylic acids.

The solvents for the kinetic studies were purified as described previously[20].

### Measurements

Rate coefficients for the base-catalysed ring fission of the substituted 2,3-diphenylcycloprop-2-en-1-ones **3** 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 ±0.05 °C. The reactions were followed at the wavelengths shown in Table I. The procedure was that described previously[20].

### Product Studies

The product of the base-catalysed ring fission of the substituted 2,3-diphenylcycloprop-2-en-1-ones **3** has been shown to be the anions of the corresponding (*E*)-2,3-diphenylacrylic acids by Bird and Hamer[8].

*We thank Dr C. W. Bird for his generous gift of the substituted 2,3-diphenylcycloprop-2-en-1-ones.*

## REFERENCES

1. Bowden K., Raja S.: *J. Chem. Soc., Perkin Trans. 2* **1999**, 39.
2. Bowden K., Horri M. V.: *J. Chem. Soc., Perkin Trans. 2* **1997**, 989.
3. Al-Najjar A., Bowden K., Horri M. V.: *J. Chem. Soc., Perkin Trans. 2* **1997**, 993.
4. Bowden K., Rumpal S.: *J. Chem. Soc., Perkin Trans. 2* **1997**, 983.
5. Bowden K., Last A. M.: *J. Chem. Soc., Perkin Trans. 2* **1983**, 351.
6. Breslow R., Eicher T., Krebs A., Peterson R. A., Posner J.: *J. Am. Chem. Soc*. **1965**, *87*, 1320.
7. Breslow R., Peterson R.: *J. Am. Chem. Soc*. **1960**, *82*, 4426.
8. Bird C. W., Hermer A. F.: *J. Chem. Soc. C* **1969**, 959.
9. Johnson C. D.: *The Hammett Equation*. Cambridge University Press, Cambridge 1973.
10. a) Greenzaid P.: *J. Org. Chem*. **1973**, *38*, 3164; b) Bover W. J., Zuman P.: *J. Chem. Soc., Perkin Trans. 2* **1973**, 786.
11. Hojo M., Utaka M., Yoshida Z.: *Tetrahedron Lett*. **1966**, *19*, 25.
12. Bowden K., Manser G. E.: *Can. J. Chem*. **1969**, *19*, 1941.
13. a) Fujita T., Nishioka T.: *Prog. Phys. Org. Chem*. **1976**, *12*, 49; b) Chapman N. B., Lee J. R., Shorter J.: *J. Chem. Soc. B* **1970**, 755.
14. Wegscheider R.: *Z. Phys. Chem*. **1889**, *30*, 593.
15. Exner O.: *Collect. Czech. Chem. Commun*. **1961**, *26*, 1.
16. Bowden K.: *Can. J. Chem*. **1963**, *41*, 2781.
17. a) Bowden K., Nadvi N. S., Ranson R. J.: *J. Chem. Res., Synop*. **1990**, 199; b) Bowden K., Nadvi N. S., Ranson R. J.: *J. Chem. Res., Miniprint* **1990**, 2474.
18. Cram D. J.: *Fundamentals of Carbanion Chemistry*. Academic Press, New York 1965.
19. Bird C. W., Briggs E. M.: *J. Chem. Soc. C* **1967**, 1265.
20. Bowden K., Last A. M.: *J. Chem. Soc., Perkin Trans. 2* **1973**, 345.