PERKIN 2

Aryl substituent effects on the thermal interconversion of cyclobutenediones and 1,2-bisketenes

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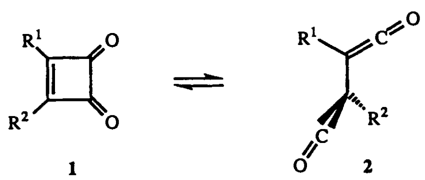
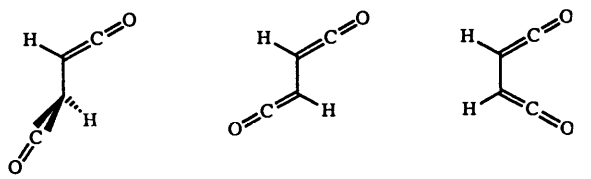
The rates and activation parameters are reported for ring closure of 1,2 bisketenes O=C=C(C_6H_4X)C($SiMe_3$)=C=O (7), generated by photolysis of the corresponding cyclobutenediones 6. The rates at 70 °C are correlated with the σ_p^+ constants of the aryl substituents by the relationship $\log k = -1.10\,\sigma_p^+ - 3.60$ ($r = 1.000$). The greater reactivity in ring closure to 6 for electron-donating aryl substituents is consistent with stabilization of the electron-deficient cyclobutenedione ring by electron donor groups, ketene stabilization by π-acceptor groups and ketene destabilization by electron-π-donor groups, as has been previously postulated based on theoretical calculations. The equilibrium concentration of 7d (X = CH_3CO) was also measured and varied from 1.6% at 69.2 °C to 9.7% at 143.1 °C, exceeding by factors of 5.4–7.5 those for 7a (X = H). This favouring of the bisketene by CH_3CO correlates closely with the effect on the reaction rates.

The interconversion of cyclobutenediones 1 and 1,2-bisketenes 2 has been of consuming interest in our laboratory.[1,2] We have found evidence that the position of the equilibrium between 1 and 2 [equilibrium (1)], and the rate constants in the forward



(1)

1 2



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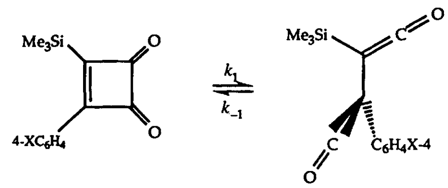
and reverse directions, can be analysed by considering the energy difference between 1 and 2 and the effect of the substituents R[1] and R[2] on the transition state for their interconversion.[1d,e,2] The energy difference between 1 and 2 has been analysed in terms of the MP2/6-31G*//MP2/6-31G* calculated thermodynamic parameters $\Delta G = 3.8$ kJ mol^{-1}, $\Delta H = 13.4$ kJ mol^{-1} and $\Delta S = 31.4$ J K^{-1} mol^{-1} for formation of 3 (R = R^2 = H), and the effects of the substituents R^1 and R^2 on the stabilities of 1 and 2.[2a] It has been found that even for the parent 3 that the twisted conformation shown is favoured over the coplanar forms 4 and 5 by 16.7 and 23.4 kJ mol^{-1}, respectively, and it is expected that for steric reasons larger substituents will tend to favour the twisted conformation even more.[2a] The twisted conformation of a derivative of 2 has been shown by X-ray crystallography.[2c]

For the case of R^2 = Ph and R^1 = Me_3Si it was found that both the cyclobutenedione 6a and the 1,2-bisketene 7a could be observed in the equilibrium mixture at elevated temperatures ([7a]/[6a] = 0.025 at 161 °C), and when 7a was generated photochemically from 6a there was a significant barrier for the reverse reaction so that the kinetics of the conversion of the bisketene back to the cyclobutadiene [equilibrium (2)] could be conveniently measured.[1e,f]

On the basis of molecular orbital calculations we proposed some time ago that the effect of substituents on the stability of ketenes could be understood on the basis that ketenes are



(2)

6a X = H
6b X = CH_3O
6c X = CH_3
6d X = CH_3CO

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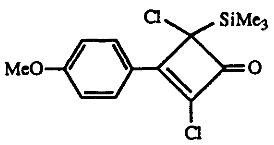
stabilized by electropositive and π-acceptor substituents, and destabilized by electronegative and π-donor substituents.[2d] Various types of evidence have been adduced to support this proposal,[1d-f,2a] and as a further test to elucidate the factors which affect the interconversion of bisketenes and cyclobutenediones we have now examined the effect of aryl substituents on this process. Included in this study are kinetic measurements of the ring closure of the 2-(trimethylsilyl)-3-aryl bisketenes 7e and 7f, where the 4-aryl substituent is either a cyclobutenedione or bisketenyl group, respectively. We have shown[1c] that these latter species are formed by photolysis of the 1,4-bis(dioxocyclobutenyl)benzene 6e (Scheme 1).

Results and discussion

Using a reported procedure,[3a] reaction of 4-substituted iodobenzenes 8b,c, (trimethylsilyl)acetylene and $Pd(OAc)_2$ gave the arylalkynes 9b,c, which were reacted with dichloroketene generated by zinc dehalogenation of CCl_3COCl[3b,c] to give the dichlorocyclobutenones 10b,c (Scheme 2). The zinc dust used was activated by heating, and 1,2-dimethoxyethane (DME) was added to reduce 1,3-chlorine migration.[3d] Hydrolysis of 10a with H_2SO_4 had given the corresponding cyclobutenedione 6a,[1e,f] but for 10b (X = MeO) the desilylated product 11 was formed. It was reasoned that desilylation occurred by protonation enhanced by the 4-MeO group as shown in Scheme 2, and to avoid this problem the hydrolyses of 10b and 10c was carried out by a modification of the procedure of Sondheimer and coworkers,[3e] using silver trifluoroacetate, and this gave the desired cyclobutenediones 6b and 6c in 57 and 54% yields, respectively.

When the reaction of 9b with CCl_3COCl and Zn was conducted in the absence of DME the product of 1,3-chlorine migration, 12, was observed.



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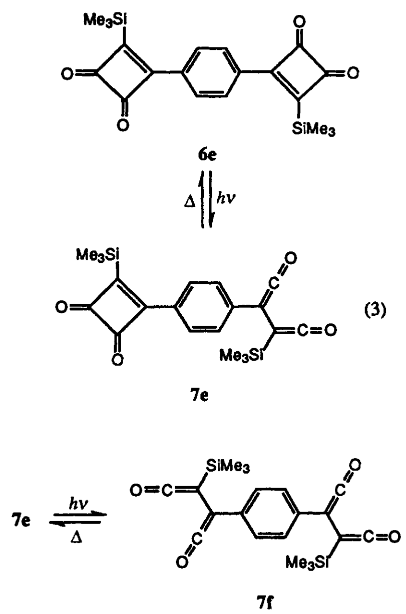
For the preparation of **6d** the initial reaction of 1,4-diiodobenzene according to Scheme 2 gave the dialkyne **9d** (X = $Me_3SiC{\equiv}C$),[1c] which on reaction with 9.1 equiv. of CCl_3COCl for 2 h gave the monocycloadduct **10d** (X = $Me_3SiC{\equiv}C$), along with the biscycloadduct[1c] in a 1:4.5 ratio. In previous work,[1c] to maximize the yield of the biscycloadduct a 16-fold excess of CCl_3COCl was used. Hydrolysis of the mixture with H_2SO_4 and chromatographic separation gave **6d** (X = CH_3CO) in 11% yield from **9d**. This reaction involved not only conversion of a dichlorocyclobutenone to a cyclobutenedione, but also the hydration with desilylation of the $Me_3SiC{\equiv}C$ group to form the CH_3CO substituent, and there is a precedent for this latter process for silylalkynes.[4]

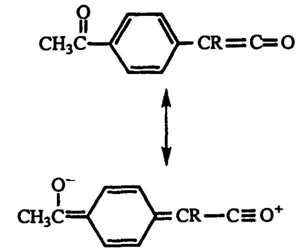
Photolysis of the cyclobutenediones **6** with 350 nm light gave the bisketenes **7**, together with residual amounts of **6** and small amounts of the alkynes **9**, established by the observation of the characteristic IR bands near 2100 cm^{-1} for **7** and 2160 cm^{-1} for **9**, and by their NMR spectra. In the ^1H NMR spectra the Me_3Si groups absorb near δ 0.25 for the alkynes **9**, 0.48 for the cyclobutenediones **6** and 0.17 for the bisketenes **7**. For the bisketenes **7a–d** the characteristic low field ^{13}C NMR absorption of C_α was observed at 178.8, 178.4, 178.3 and 177.5, respectively, for the silylketene moiety and 202.2, 204.1, 203.1 and 198.1, respectively, for the arylketene moiety. The high field absorption of C_β was observed at 7.9, 7.4, 7.1 and 7.0, and 33.5, 31.9, 32.6 and 34.2, respectively, for the silyl and arylketene moieties, respectively. Distinctive absorptions are also observed for the aryl groups and the CH_3 groups of the substituents.



Scheme 1

It is striking that the carbonyl carbon C_α of the silylketenyl moieties averages 24.2 ppm upfield from that of the arylketenyl moieties in the same molecule. In a recent analysis of the NMR spectra of silylketenes this effect was attributed to σ_π–p_π electron-donation from the C_α–Si bond to the in-plane p orbital at C_α.[5]

Upon prolonged photolysis the ratios of [**6**]:[**7**] stayed approximately constant, while the amounts of the alkynes **9** gradually increased. This behaviour may indicate that a photostationary state is reached, in which **6** and **7** are interconverted photochemically, while in a competing reaction photochemical decarbonylation of **7** to the alkynes **9** occurs. The cyclobutenediones **6b–d** show UV spectra with λ_{max} at 310, 288 and 277 nm, respectively, while the bisketenes **7a–c** show λ_{max} near 257 nm, but **7d** (X = CH_3CO) shows λ_{max} 289. This longer wavelength absorption for the acyl-substituted bisketene is consistent with conjugation of the acyl group with the adjacent ketenyl group as shown in **13**. Analogous behaviour has been proposed



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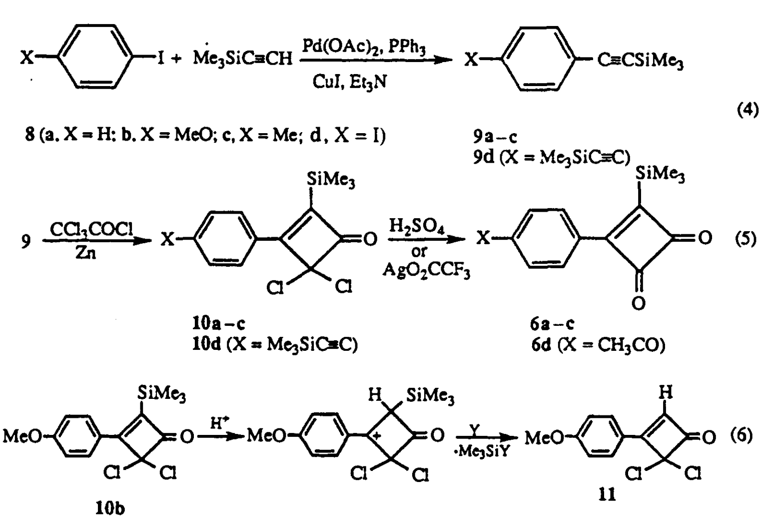
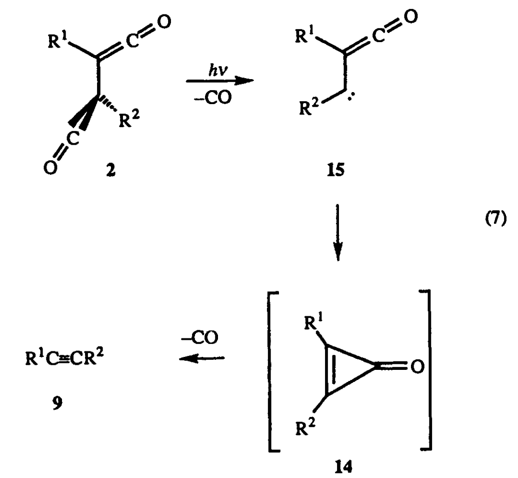
for α-acylketenes.[1a,2d] The longer wavelength absorption of the cyclobutenediones **6b** and **6c** substituted with electron-donor groups MeO and Me, respectively, is consistent with electron-donation to the electron-deficient cyclobutenedione.

The photochemical[6a] and thermal[6b] conversion of 1,2-bisketenes to alkynes has been observed previously, and for the



Scheme 2

examples $R^1 = R^2 = EtO$ and $R^1 = R^2 = H$, formation of cyclopropenones **14** have been observed at low temperatures and the formation of **14** has been proposed to occur *via* ketenylcarbenes **15** (Scheme 3).[7] However, in other studies[1b–f] and in the current

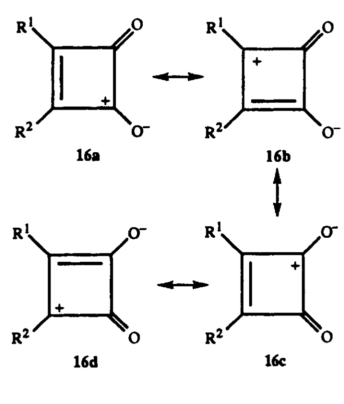


Scheme 3

work, cyclopropenones were not detected, although their intervention as unobserved intermediates cannot be excluded.

Heating of the bisketenes **7b–d** resulted in the reformation of the cyclobutenediones **6**, as observed by both UV and ^1H NMR spectroscopy. For determination of the rates of ring closure the bisketenes **7b–d** were generated by photolysis of the cyclobutenediones in isooctane using 350 nm light. Conversions of 70–90% were achieved. Kinetic studies were carried out by observing the change in the UV absorption of these solutions at different temperatures, to give the rate constants and activation parameters collected in Table 1. For certain cases the rate constants were also measured in $CDCl_3$ solutions by ^1H NMR spectroscopy to verify that the processes observed corresponded to the desired ring closure.

For **7a**, **7b**, **7d**, **7e** and **7f** at 70 °C the rates determined by ^1H NMR spectroscopy in $CDCl_3$ exceed the rates in isooctane or hexane (Table 1) by factors of 4.3, 3.2, 1.5 and 4.3, respectively, or an average factor of 2.9. This agrees with our previously measured[1d] solvent dependence of the rate of conversion of bisketenes **2** ($R^1 = R^2 = Ph$; $R^1 = Ph$, $R^2 = H$) to the corresponding cyclobutenediones, which also showed greater rates in the more polar $CDCl_3$ compared with isooctane or hexane, by factors of 3.3 to 4.2. This enhancement of the rate by solvent polarity may be attributed to the greater polarity of the



cyclobutenediones compared with the bisketenes, owing to the electron-deficient character of the former as represented in the resonance structures **16**. Recent measurements of the ^{17}O NMR spectra of cyclobutenediones and calculations of natural

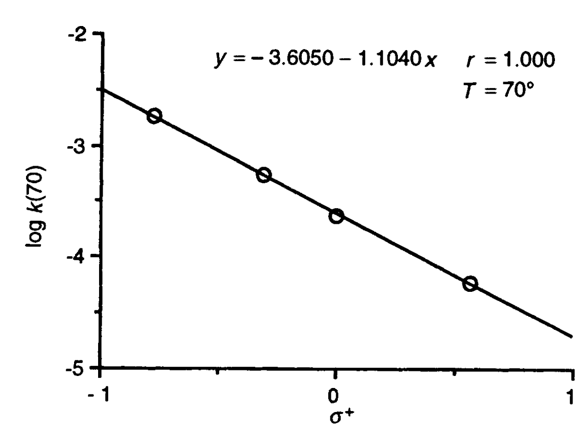


Fig. 1 Correlation of log *k* for ring closure of **7a–d** *vs.* substituent constants.

atomic charges, confirm the charge distribution shown in **16**, and provide an estimate of a net charge of +1.1 distributed among the four carbon atoms ($R^1 = R^2 = CH_3$).[8]

For comparison of the rates of ring closure of **7a–d** the rate constants for this process at 70.0 °C in isooctane or hexane were interpolated, as reported in Table 1. This temperature lies within the experimental range of observation for all four substrates and gives the correlation $\log k = (-1.10 \pm 0.01)\ \sigma_p^+ - 3.60 \pm 0.01$ ($r = 1.000$) with the Brown–Hammett substituent parameters σ_p^+ (Fig. 1).[9] At other temperatures the correlation is significantly less precise due to the different activation parameters for the different substrates, and the σ_p^+ constant of the CH_3CO substituent of 0.57[9] was derived from a different data set than those for the MeO and Me groups.

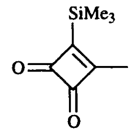
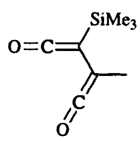
The rate constant in isooctane of the first ring closure of the tetraketene **7f** to give the bisketene **7e** (Scheme 1) at 70.0 °C is calculated to be $1.24 \times 10^{-3}\ s^{-1}$, which is 5.2 times greater than the rate of $2.39 \times 10^{-4}\ s^{-1}$ measured in hexane[1e] for the parent **7a** (Table 1). The same rate factor is found in $CDCl_3$ (Table 1). This may be interpreted as resulting from a destabilization of the tetraketene **7f** due to an unfavourable interaction of the two bisketenyl units in **7f**, combined with a stabilization of **7e** due to π-donation from the ketenyl group to the electron-deficient cyclobutenedione unit, analogous to that shown in **13**. This also accounts for the lower reactivity in the second ring closure of **7e** to form **6e** by factors of 20 (isooctane, 70.0 °C) and 75 ($CDCl_3$, 69.5 °C) compared with the reactivity in the first ring closure.

The rate of the first ring closure of **7f** in $CDCl_3$ at 69.5 °C is exceeded by that of the 4-MeO derivative **7b** at 69.2 °C in $CDCl_3$ by a factor of only 1.08, while in isooctane at 70.0 °C the ratio is 1.47. In view of the correlation of the rates of ring closure with the σ_p^+ parameters this leads to the somewhat surprising conclusion that the bisketenyl group in **7f** is a π-electron donor of comparable power to the MeO group. The π-donating ability of the ketenyl group is well recognized, as illustrated in **13**,[1a,2d] and these results provide a quantitative measure, equivalent to the σ_p^+ value of the 4-MeO group of −0.78.

The rate ratio $k(\mathbf{7e})/k(\mathbf{7d})$ in $CDCl_3$ at 70.0 °C for ring closure of the second bisketenyl unit in **7e** compared with the value for the 4-CH_3CO substituted derivative **7d** is 0.71, while in isooctane this ratio is 1.06, indicating that the cyclobutenedione substituent in **7e** is comparable in electron-accepting ability to acetyl. The electron-accepting ability of the cyclobutenedione moiety arises from the electron-deficient character shown in **16a–d**,[2a,8a] and these results provide a quantitative measure of this property, equivalent to the σ_p^+ value of 0.57 for acetyl.[9]

The equilibrium constant at different temperatures for the

Table 1 Kinetics of conversion of bisketenes **7** to cyclobutenediones **6**

X	Solvent	T/°C	k_{obs}/s^{-1}	$\Delta H^{\ddagger}$/kJ mol^{-1}	$\Delta S^{\ddagger}$/J K^{-1} mol^{-1}
MeO (**7b**)	Isooctane	75.3	$(2.71 \pm 0.01) \times 10^{-3}$		
		70.0[a]	1.82×10^{-3}		
		65.5	$(1.20 \pm 0.04) \times 10^{-3}$		
		50.4	$(3.10 \pm 0.13) \times 10^{-4}$		
		25.0[a,b]	2.43×10^{-5}	78.9	−69
	$CDCl_3$	69.2	$(5.80 \pm 0.12) \times 10^{-3}$		
Me (**7c**)	Isooctane	74.5	$(8.95 \pm 0.05) \times 10^{-4}$		
		70.0[a]	5.50×10^{-4}		
		67.2	$(4.43 \pm 0.03) \times 10^{-4}$		
		49.2	$(6.12 \pm 0.02) \times 10^{-5}$		
		25.0[a,c]	2.96×10^{-6}	96.4	−54
CH_3CO (**7d**)	Isooctane	84.0	$(1.95 \pm 0.05) \times 10^{-4}$		
		73.3	$(8.00 \pm 0.10) \times 10^{-5}$		
		70.0[a,d]	5.94×10^{-5}		
		25.0[a,d]	2.73×10^{-7}	82.8	−86
	$CDCl_3$	100.5	$(1.82 \pm 0.07) \times 10^{-3}$		
		80.7	$(3.17 \pm 0.37) \times 10^{-4}$		
		70.5	$(8.89 \pm 0.21) \times 10^{-5}$		
		70.0[a]	1.03×10^{-4}		
		25.0[a,e]	5.31×10^{-7}	103.2	−23
H[f] (**7a**)	Hexanes	82.4	7.78×10^{-4}		
		70.0[a]	2.39×10^{-4}		
		65.4	1.62×10^{-4}		
		50.0	3.54×10^{-5}		
		25.0[a,g]	1.93×10^{-6}	88.3	−57
	$CDCl_3$	70.5	1.02×10^{-3}		
 (**7e**)	Isooctane	89.1	$(4.30 \pm 0.12) \times 10^{-4}$		
		78.1	$(1.46 \pm 0.03) \times 10^{-4}$		
		70.0[a]	6.31×10^{-5}		
		25.0[a,h]	2.58×10^{-7}	100.8	−33
	$CDCl_3$	100.0	$(1.68 \pm 0.08) \times 10^{-3}$		
		80.7	$(2.43 \pm 0.04) \times 10^{-4}$		
		70.0[a]	7.30×10^{-5}		
		69.5	$(7.10 \pm 0.10) \times 10^{-5}$		
		25.0[a,i]	2.15×10^{-7}	118.7	19
 (**7f**)	Isooctane	78.1	$(2.21 \pm 0.17) \times 10^{-3}$		
		70.0[a]	1.24×10^{-3}		
		68.7	$(1.13 \pm 0.05) \times 10^{-3}$		
		58.8	$(5.45 \pm 0.20) \times 10^{-4}$		
		25.0[a,j]	3.07×10^{-5}	67.5	−105
	$CDCl_3$	70.0[a]	5.32×10^{-3}		
		69.5	$(5.35 \pm 0.07) \times 10^{-3}$		
		56.6	$(1.55 \pm 0.05) \times 10^{-3}$		
		34.6	$(2.02 \pm 0.02) \times 10^{-4}$		
		25.0[a,k]	7.04×10^{-5}	79.1	29

[a] Calculated from rates at other temperatures. [b] Ln $k_{obs} = -9.820/T + 22.3$, $E_{act} = 81.6$ kJ mol^{-1}. [c] Ln $k_{obs} = -11.900/T + 27.3$, $E_{act} = 98.9$ kJ mol^{-1}. [d] Ln $k_{obs} = -10.330/T + 20.3$, $E_{act} = 85.9$ kJ mol^{-1}. [e] Ln $k_{obs} = -11.600/T + 24.6$, $E_{act} = 99.4$ kJ mol^{-1}. [f] Ref. 1(*e*). [g] Ln $k_{obs} = -10.960/T + 23.7$, $E_{act} = 91.1$ kJ mol^{-1}. [h] Ln $k_{obs} = -12.500/T + 26.75$, $E_{act} = 103.9$ kJ mol^{-1}. [i] Ln $k_{obs} = -13.300/T + 29.2$, $E_{act} = 110.6$ kJ mol^{-1}. [j] Ln $k_{obs} = -8.430/T + 18.0$, $E_{act} = 70.1$ kJ mol^{-1}. [k] Ln $k_{obs} = -9.840/T + 23.4$, $E_{act} = 81.8$ kJ mol^{-1}.

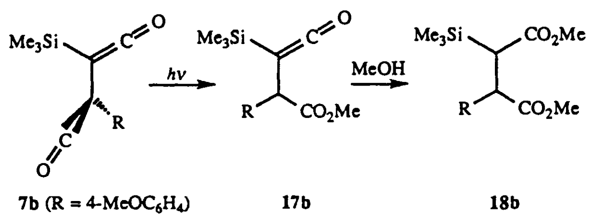
interconversion of the cyclobutenedione **6d** to the bisketene **7d** (X = CH_3CO) was also determined by heating $CDCl_3$ solutions of **6d** until equilibrium was obtained, then rapidly cooling the solution and measuring the respective concentrations of **6d** and **7d** from the areas of their ^1H NMR CH_3 and $(CH_3)_3Si$ signals, as reported in Table 2. Comparison of these data with those obtained similarly for **6a** and **7a**[1e,f] reveals that for X = CH_3CO the equilibrium constant for formation of the bisketene **7d** is significantly larger than that for formation of **7a** (X = H); by factors of 7.5 (143.1 °C), 7.3 (100.5 °C) and 5.4 (25.0 °C). The values of ΔG° (25 °C) are 13.8 and 18.4 kJ mol^{-1}, respectively, and the ρ^+ value for the dependence of log K on the substituent constants is 1.25. Thus the ratio of the magnitudes of the ρ^+ values for the rates and equilibrium constants for ring closure is 0.89. This value is the same as that reported by Arnett *et al.*,[10] for the slope of a plot of free energies of activation of solvolysis of alkyl chlorides in ethanol *versus* the heats of ionization of the same chlorides in SbF_5–solvent mixtures.

For further characterization of the bisketene **7b** reaction with MeOH followed by fast removal of the excess solvent led to the formation of the monoketene **17b** which was purified by chromatography and identified by its spectral properties (Scheme 4). Further reaction with MeOH gave the diastereomeric succinates **18b**. This behaviour parallels that found previously for **7a** (R = Ph), in which the *erythro* and *threo* succinates **18a** were formed in a 2:1 ratio.[1e,f] The *erythro* and *threo* succinates **18b** were formed in a 3:2 ratio as shown by ^1H NMR analysis and were separated by column chromatography and identified by comparison of the NMR spectra with those previously obtained for **18a**.[1f]

Table 2 Thermal equilibration of **6d** and **7d**

T/°C	**7d**:**6d**	K^a
143.1	9.7:90.3	1.07×10^{-1}
100.5	5.0:95.0	5.12×10^{-2}
69.2	1.6:98.4	1.51×10^{-2}
25.0[b]	0.3:99.7	3.26×10^{-3}

[a] Ln $K = 6.89 - 3760/T$, $r = 0.974$, $\Delta G°$ (25 °C) = 13.8 kJ mol^{-1}, $\Delta H° = 30.1$ kJ mol^{-1}, $\Delta S° = 54.8$ J K^{-1} mol^{-1}. [b] Extrapolated.



7b (R = 4-MeOC$_6$H$_4$) **17b** **18b**

Scheme 4

Experimental

General procedures

Most of the reagents and solvents were obtained from Aldrich or BDH. Diethyl ether was distilled from sodium–benzophenone. All reactions were carried out in oven dried glassware and $CDCl_3$ used as a reaction solvent was dried over 4A molecular sieves. NMR spectra were measured using Varian Germini 200 and XL-400 spectrometers. Chemical shifts are given in ppm; J values are given in Hz. IR spectra were measured using Nicolet DX FTIR and Perkin-Elmer 882 instruments. Mass spectra were obtained on a VG 70-2505 instrument. The sonicator was a Branson Model 1200. The UV absorption and kinetic data were obtained using a Varian 210 instrument. Photolyses were carried out with a RPR-100 Rayonet photoreactor.

1-(4′-Methoxyphenyl)-2-(trimethylsilyl)acetylene (9b).[11] To a 100 ml flask equipped with a condenser was added successively Et_3N (60 ml), 4-iodoanisole (2.34 g, 0.01 mol), CuI (41 mg, 0.2 mmol), PPh_3 (111 mg, 0.4 mmol), $Pd(OAc)_2$ (50 mg, 0.2 mmol) and (trimethylsilyl)acetylene (1.18 g, 0.012 mol). The reaction mixture was heated at 80 °C for 5 h. After cooling the reaction mixture was filtered and the collected salts were washed with diethyl ether, and the combined filtrate was evaporated to give crude **9b** as a yellow liquid: δ_H($CDCl_3$) 0.24 (s, 9 H, Me_3Si), 3.78 (s, 3 H, OCH_3), 6.80 and 7.90 (d of d, 4 H, Ar).

1-(4′-Methoxyphenyl)-2-(trimethylsilyl)-3-oxo-4,4-dichlorocyclobut-1-ene (10b). To a 100 ml round-bottom flask was added flame-treated zinc dust (2 g, 0.031 mol) and the alkyne **9d** (1.0 g, 5 mmol) in 20 ml diethyl ether, and CCl_3COCl (2 ml, 18 mmol) in 10 ml diethyl ether was added dropwise over 3 h with stirring. The reaction mixture was stirred overnight, filtered through silica gel and evaporated. Chromatography on silica gel with 1:9 EtOAc–hexane gave the 1,3-chlorine-migration product **12**: δ_H($CDCl_3$) 0.22 (s, 9 H, Me_3Si), 3.89 (s, 3 H, OCH_3), 7.03 and 7.98 (d of d, 4 H, Ar); δ_C($CDCl_3$) −1.9, 56.2, 115.2, 115.4, 121.8, 132.8, 133.2, 164.0, 168.8, 182.3; EIMS m/z 314 (M^+, 57%), 279 ($M^+ - Cl$, 46), 252 ($M^+ - Cl$, CO, 25), 178 ($M^+ - Cl$, Me_3Si, CO, 54), 73 (Me_3Si^+, 100).

From a similar reaction with added DME **10b** was obtained: δ_H($CDCl_3$) 0.38 (s, 9 H, Me_3Si), 3.92 (s, 3 H, OCH_3), 7.03 and 7.90 (d of d, 4 H, Ar); δ_C($CDCl_3$) −0.9, 56.2, 97.7, 115.4, 121.2, 133.1, 147.4, 164.2, 180.2, 183.2; ν($CDCl_3$)/cm^{-1} 1771; EIMS m/z 314 (M^+, 58%), 271 ($M^+ - CO - CH_3$, 48), 251 ($M^+ - Cl -$ CO, 22), 73 (Me_3Si^+, 100) (HRMS calc. for $C_{14}H_{16}Cl_2O_2Si$ 380.0586; found 380.0580).

1-(4′-Methoxyphenyl)-2-(trimethylsilyl)cyclobut-1-ene-3,4-dione (6b). To a 10 ml flask containing **10b** (0.5 g, 1.4 mmol) in 5 ml EtOAc was added silver trifluoroacetate (1.7 g, 7.7 mmol) in 3 ml EtOAc, and the solution was refluxed for 2 h. The mixture was filtered and the solvent evaporated, and the residue was chromatographed with silica gel using 5:95 EtOAc–hexane to give **6b** as a yellow solid, mp 114–115 °C: δ_H($CDCl_3$) 0.47 (s, 9 H, Me_3Si), 3.92 (s, 3 H, CH_3O), 7.08 and 7.99 (d of d, 4 H, Ar); δ_C($CDCl_3$) −1.91, 56.8, 116.0, 123.0, 133.1, 165.2, 198.8, 199.6, 200.0, 201.4; ν($CDCl_3$)/cm^{-1} 1793, 1774 (C=O); $\lambda_{max}^{isooctane}$/nm 310; EIMS m/z 260 (M^+, 23%), 204 ($M^+ - 2CO$, 64), 189 ($M^+ - 2CO$, CH_3, 100), 73 (Me_3Si^+, 48) (HRMS calc. for $C_{14}H_{16}O_3Si$ 260.0869; found 260.0856).

2-(Trimethylsilyl)-3-(4′-methoxyphenyl)buta-1,3-diene-1,4-dione (7b). A degassed solution of **6b** (10 mg, 0.04 mmol) in 0.6 ml $CDCl_3$ in a sealed NMR tube was photolysed for 1 h with 350 nm light, and the ^1H NMR spectrum showed the formation of **7b** as 94% of the product mixture, based on the integration of the Me_3Si signals: δ_H($CDCl_3$) 0.17 (s, 9 H, Me_3Si), 3.79 (s, 3 H, OCH_3), 6.95 and 7.03 (d of d, 4 H, Ar); δ_C($CDCl_3$) −0.78, 7.36, 31.9, 55.4, 114.2, 123.1, 124.9, 156.5, 178.4, 204.1; ν($CDCl_3$)/cm^{-1} 2094; $\lambda_{max}^{isooctane}$/nm 257.

2-(Trimethylsilyl)-3-(4′-methoxylphenyl)-3-methoxycarbonyl)prop-1-en-1-one (17b). An NMR tube containing cyclobutenedione **6b** (60 mg, 0.23 mmol) and MeOH (9 µl, 0.23 mmol) in 0.5 ml $CDCl_3$ was photolysed for 140 min with 350 nm light and showed the formation of **17b** in greater than 90% yield as indicated by the ^1H NMR integration. This was purified by radial chromatography on silica gel with 1% ethyl acetate in hexane to give **17b**: δ_H($CDCl_3$) 0.02 (s, 9 H, Me_3Si), 3.67 (s, 3 H, MeO), 3.79 (s, 3 H, MeO), 3.95 (s, 1 H, CHAr), 6.85 and 7.29 (d of d, 4, Ar); δ_C($CDCl_3$) 16.9, 46.4, 53.1, 55.2, 113.7, 129.0, 130.6, 158.9, 173.6, 179.8; ν($CDCl_3$)/cm^{-1} 2089 (C=C=O), 1725 (C=O); EIMS m/z 292 (M^+, 9%), 277 ($M^+ -$ CH_3, 18), 249 ($M^+ - CH_3$, CO, 10), 233 ($M^+ - CO_2Me$, 100), 73 (Me_3Si^+, 80) (HRMS calc. for $C_{15}H_{20}O_4Si$ 292.1131; found 292.1125).

Dimethyl 2-(4′-methoxyphenyl)-3-(trimethylsilyl)succinate (18b). To the NMR tube containing **17b** prepared as above, was added 10 µl MeOH and the tube was kept at 0 °C for 3 h. The ^1H NMR spectrum of the solution showed the presence of the *erythro* and *threo* isomers of **18b** in a 3:2 ratio. The solvent was evaporated and the isomers were separated by column chromatography on silica gel to give first *erythro* **18b**, colourless crystals, mp 53.0–54.5 °C: δ_H($CDCl_3$) 0.12 (s, 9 H, Me_3Si), 3.05 (d, 1 H, J 12.4, C*H*SiMe$_3$), 3.40 (s, 3 H, OCH_3), 3.62 (s, 3 H, OCH_3), 3.77 (s, 3 H, OCH_3), 3.97 (d, 1 H, J 12.4, C*H*Ar), 6.81 and 7.27 (d of d, 4 H, Ar); δ_C($CDCl_3$) −2.0, 41.2, 48.9, 51.0, 52.1, 55.2, 113.8, 128.8, 131.1, 158.7, 173.3, 173.5; ν($CDCl_3$)/cm^{-1} 1728, 1719 (CO_2Me); EIMS m/z 324 (M^+, 2%), 309 ($M^+ - CH_3$, 13), 292 ($M^+ - CH_3OH$, 26), 265 ($M^+ - CO_2CH_3$, 10), 161 ($M^+ - CO_2Me$, TMS, OCH_3, 100), 73 (Me_3Si^+, 38) (HRMS calc. for $C_{16}H_{24}O_5Si$ 324.1393; found 324.1386). Further chromatography gave *threo*-**18b**: δ_H($CDCl_3$) −0.19 (s, 9 H, Me_3Si), 2.92 (d, 1 H, J 12.4, C*H*SiMe$_3$), 3.59 (s, 3 H, OCH_3), 3.68 (s, 3 H, OCH_3), 3.79 (s, 3 H, OCH_3), 4.03 (d, 1 H, J 12.4, C*H*Ar), 6.84 and 7.22 (d of d, 4 H, Ar); δ_C($CDCl_3$) −2.0, 41.1, 49.5, 51.3, 52.2, 55.2, 114.1, 128.9, 129.7, 159.2, 174.6, 174.9; IR ν($CDCl_3$)/cm^{-1} 1729, 1713 (CO_2Me); EIMS m/z 324 (M^+, 2%), 309 ($M^+ - CH_3$, 14), 292 ($M^+ - CH_3OH$, 23), 277 ($M^+ - CH_3OH$–CH_3, 16), 265 ($M^+ - CO_2CH_3$, 20), 161 ($M^+ - CO_2CH_3$, TMS, OCH_3, 100), 73 (Me_3Si^+, 34) (HRMS found 324.1378).

1-(4′-Methylphenyl)-2-(trimethylsilyl)cyclobut-1-ene-3,4-dione (6c). **6c** was prepared by the same procedures followed for **6b** using 4-iodotoluene as the starting material; mp 89–90 °C: δ_H($CDCl_3$) 0.47 (s, 9 H, Me_3Si), 2.47 (s, 3 H, CH_3Ar), 7.37 and 7.88 (d of d, 4 H, Ar); δ_C($CDCl_3$) −1.89, 21.9, 126.4, 129.5, 130.0, 144.9, 198.1, 199.0, 200.9, 201.1; $\lambda_{max}^{isooctane}$/nm 288; EIMS m/z 244 (M^+, 17%), 188 ($M^+ - 2CO$, 45), 173 ($M^+ - 2CO$, CH_3, 100), 73 (Me_3Si^+, 27) (HRMS calc. for $C_{14}H_{16}O_2Si$ 244.0919; found 244.0911).

2-(Trimethylsilyl)-3-(4′-methylphenyl)buta-1,3-diene-1,4-dione (7c). Photolysis of **6c** (20 mg, 0.08 mmol) in $CDCl_3$ in an

NMR tube with 350 nm light for 2.5 h gave a 76% conversion to **7c**: δ_H($CDCl_3$) 0.20 (s, 9 H, Me_3Si), 2.32 (s, 3 H, CH_3Ar), 7.00 and 7.13 (d of d, 4 H, Ar); δ_C($CDCl_3$) −0.81, 7.09, 21.0, 32.6, 123.7, 128.5, 129.5, 134.1, 178.3, 203.0; ν($CDCl_3$)/cm^{-1} 2094; $\lambda_{max}^{isooctane}$/nm 257.

1-(4′-Acetylphenyl)-2-(trimethylsilyl)cyclobut-1-ene-3,4-dione (6d). To a dry, 100 ml three-necked flask under nitrogen was added flame-treated zinc dust (1.5 g, 0.02 mol), 1,4-bis(trimethylsilylethynyl)benzene **9d** (1.0 g, 3.7 mmol)[1c] and 10 ml anhydrous diethyl ether. Trichloroacetyl chloride (1.5 g, 0.008 mol) dissolved in 10 ml diethyl ether was added dropwise for 30 min and the reaction mixture was stirred for another 1.5 h. The product was filtered through Celite to remove unreacted zinc and washed with diethyl ether and the solvent was evaporated. The residue was separated by flash chromatography by elution with 10% ethyl acetate and 90% hexane to give **10d** as a yellow solid: δ_H($CDCl_3$) 0.26 (s, 9 H, Me_3Si), 0.35 (s, 9 H, Me_3Si), 7.61 and 7.82 (d of d, J 8.6, 4 H, Ar); δ_C($CDCl_3$) −1.02, 0.42, 91.7, 104.4, 127.6, 128.2, 128.5, 128.7, 130.3, 133.0, 178.4, 182.8; ν($CDCl_3$)/cm^{-1} 2158, 1785; EIMS m/z 380 (M^+, 57%), 365 ($M^+ - CH_3$, 16), 337 ($M^+ - CO - CH_3$, 25), 73 (Me_3Si^+, 100) (HRMS calc. for $C_{18}H_{22}Cl_2OSi$ 380.0586; found 380.0580).

The product above was dissolved in 10 ml $CHCl_3$ in a 50 ml round-bottom flask with magnetic stirring, and 6 ml concentrated sulfuric acid was added and the flask was heated to 87 °C, the mixture was stirred for 0.5 h, poured into 30 ml ice–water, worked up as in the preparation of **6b** and purified by flash chromatography with 10% EtOAc in hexane to give pure triketone **6d** as a yellow oil which later solidified (110 mg, 0.40 mmol, 11% from **9d**), mp 98–99 °C: δ_H($CDCl_3$) 0.40 (s, 9 H, Me_3Si), 2.60 (s, 3 H, CH_3CO), 7.94 and 8.05 (d of d, J 8.7, 4 H, Ar); δ_C($CDCl_3$) −1.90, 26.7, 128.8, 129.3, 132.6, 134.0, 196.9, 197.0, 198.0, 199.9, 205.0; ν($CDCl_3$)/cm^{-1} 1779, 1690 (C=O), 1549 (C=C); EIMS m/z 272 (M^+, 20%), 216 ($M^+ - 2CO$, 42), 201 ($M^+ - 2CO - CH_3$, 100), 158 ($M^+ - 3CO - 2CH_3$, 18) (HRMS calc. for $C_{15}H_{16}O_3Si$ 272.0869; found 272.0872).

2-(Trimethylsilyl)-3-(4′-acetylphenyl)buta-1,3-diene-1,4-dione (7d). A sample of **6d** (60 mg) in 0.8 ml $CDCl_3$ in an NMR tube was degassed for 20 min and then sealed. The sealed sample was photolysed at 350 nm for 5 h, and the ^{1}H NMR spectrum indicated that **7d** was formed with 95% conversion: δ_H($CDCl_3$) 0.14 s, 9 H, $SiMe_3$), 2.50 (s, 3 H, CH_3CO), 7.14 and 7.89 (d of d, J 8.7, Ar); δ_C($CDCl_3$) 0.8, 7.0, 26.3, 34.2, 123.4, 129.1, 133.5, 138.4, 177.5, 196.8, 198.1; ν($CDCl_3$)/cm^{-1} 2100 (C=C=O) and 1601; $\lambda_{max}^{isooctane}$/nm 289. The decarbonylated alkyne 4-$CH_3COC_6H_4C{\equiv}CSiMe_3$[11] was separated after heating **7d** and identified by ^{1}H NMR analysis: δ_H($CDCl_3$) 0.27 (s, 9 H, Me_3Si), 2.60 (s, 3 H, CH_3CO), 7.54 and 7.89 (each d, J 8.7, Ar).

Kinetic measurements

A 2×10^{-5} M solution of cyclobutenedione **6d** (X = CH_3CO) was prepared by injecting 2 µl of a 0.01 M solution of the dione in CH_3CN into 1.2 ml of isooctane. The solution was irradiated for 8 min using 350 nm light, and the UV spectrum showed a shift in the λ_{max} from that of the dione at 277 nm to that of the bisketene at 289 nm. The kinetics of the ring closure were measured by monitoring the decrease in the absorption of the bisketene at 310 nm, where the largest change occurred. The other bisketene solutions were prepared similarly, and for **7b** (X = MeO) the decrease in the bisketene λ_{max} at 256 nm, reforming the dione λ_{max} at 310 nm, was monitored, while for **7c** (X = Me) the rates were monitored by observing either the decrease in the λ_{max} of the bisketene at 257 nm, or the increase in the dione absorption at 288 nm.

Determination of equilibrium constants between 6d and 7d

An NMR tube containing 15 mg **6d** in 0.8 ml $CDCl_3$ was degassed for 15 min then sealed. The NMR tube was heated in refluxing hexane (69.2 °C), water (100.5 °C) and styrene (143.1 °C) until equilibrium was reached. The solution was cooled quickly and equilibrium concentrations were measured by ^{1}H NMR integrations of signals at δ 2.60 and 0.40 of **6d** and δ 2.50 and 0.14 of **7d**. The calculated half-life of the interconversion at 25 °C is 15 days and so no significant change in the relative concentrations is expected during the NMR measurements.

Kinetics of the conversion of 7f to 7e and 6e

Samples of **7f** were prepared by injecting 10 µl aliquots of a 0.0025 M solution of **6e**[1c] in CH_3CN into 1.2 ml of isooctane and irradiating for 1 min at 350 nm. The rates of conversion of **7f** to **7e** were then measured by monitoring either the decrease in the absorption at 287 nm or the increase in the absorption of **7f** at 357 nm. Good agreement between the measurements was found. The further conversion of **7e** into **6e** was monitored by the decrease at 357 nm.

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