Generation of 1,2-Bisketenes from Cyclobutene-1,2-diones by Flash Photolysis and Ring Closure Kinetics[1a]

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Received July 8, 1997[⊗]

Abstract: The interconversion of cyclobutene-1,2-diones (**1**) and 1,2-bisketenes (RC=C=O)$_2$ (**2**) has been surveyed for different combinations of substituents R = H, Me, *t*-Bu, Ph, Me$_3$Si, CN, Cl, Br, R^{1}O, alkynyl, and PhS. The bisketenes **2** have been generated by flash photolysis, and the kinetics of their conversion to **1** have been studied by time-resolved infrared and ultraviolet spectroscopy. The rate constants of the ring closure of **2** are correlated by the ketene stabilization parameters (*SE*) and with calculated barriers. The rate constant of ring closure of the di-*tert*-butyl bisketene **2g** to cyclobutenedione **1g** is only 40 times smaller than for the dimethyl analogue, showing a rather modest steric barrier. The quinoketene **2s** has a fast rate of ring closure, but not as fast as anticipated on the basis of calculated geometric and thermodynamic factors. A lag in the attainment of aromatic stabilization in the transition structure for ring closure is a possible cause of this diminished reactivity.

The photochemical ring opening of cyclobutene-1,2-diones (**1**) to give 1,2-bisketenes (**2**) was discovered simultaneously by Mallory and Roberts[1b] and by Blomquist and LaLancette[1c] in 1961 (eq 1). The 1,2-bisketenes were not directly observed
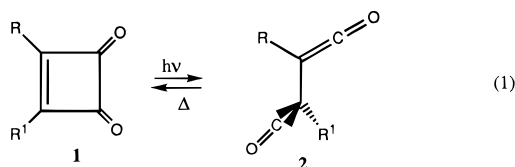
but were inferred as reactive intermediates on the basis of the products formed. Since that time, this technique has been utilized to generate several 1,2-bisketenes, but usually, these species have only been observed at low temperatures, often in matrices because of their facile thermal ring closure back to **1**.[2]

Recently, we found that for R = R^1 = Me$_3$Si the 1,2-bisketene **2** was thermodynamically stable relative to the cyclobutenedi-

ones **1**, while those with one silyl substituent were less stable than the corresponding cyclobutenediones but were relatively long lived at room temperature.[3] This opened the way for extensive studies[4] of the spectroscopic and chemical properties of 1,2-bisketenes **2**, including an X-ray crystallographic structure determination,[4f] which showed a 119° angle between the adjacent ketenyl groups in an analogue of **2**, confirming the twisted structure predicted[3c,f] on the basis of theoretical studies and dipole moment measurements.

In a preliminary study,[3d] we have examined the formation of several 1,2-bisketenes **2** by the photolysis of cyclobutenediones **1** and have used time-resolved infrared spectroscopy (TRIR) for the observation of some of these species. This technique[5] is well suited for the observation of such 1,2-ketenes because of their strong IR bands near 2100 cm^{-1}, a region that is free from absorption by most other functional groups. This method is also useful for the measurement of fast reaction kinetics and

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[⊗] Abstract published in *Advance ACS Abstracts,* December 1, 1997.
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was applied to the determination of the rate constants for ring closure in selected examples.[3d] We have also used UV spectroscopy for the measurement of the rates of thermal conversion of the 1,2-bisketenes **2** back to cyclobutenediones **1** in examples where the reactions are slower[3b,d,4b] and now report a survey of this process for representative structural types of 1,2-bisketenes. These include ketenes with CN,[6] Br,[7] alkynyl,[8] thio,[9] and alkoxy[10] substituents and permit a quantitative test of previously derived ketene substituent parameters (SE)[11a,b] and studies of substituent effects on cyclobutenediones.[3c,11c] As a test of steric effects on the interconversion of eq 1, the crowded di-*tert*-butylcyclobutene-1,2-dione (**1g**) has also been prepared and its interconversion with the bisketene $(t\text{-BuC=C=O})_2$ (**2g**) studied.

Results

The cyclobutenediones except for **1g,o** are known compounds.[1-3,12] The bis(*t*-Bu) derivative **1g** was made by two independent routes, as shown in eqs 2 and 3. The route of eq


(2)

(3)
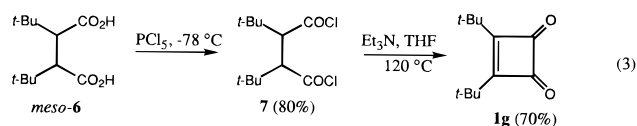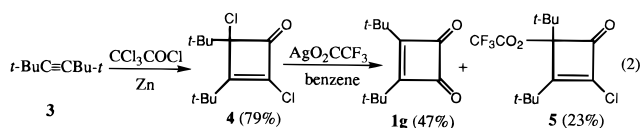
3 from *meso*-2,3-di-*tert*-butylsuccinic acid (**6**)[13] presumably involved the bisketene **2g** as an intermediate. Evidence for the formation of **2g** was obtained by the reaction of **7** with DMAP at room temperature, which gave spectral evidence for the presence of 10% of **2g** together with the known[3a] anhydride **8** (eq 4). The structure of **2g** was indicated by the IR band at

2101 cm^{-1} and the ^{1}H NMR signal at δ 1.17. Hydration by adventitious H$_2$O evidently led to **8**. As described below photolysis of **1g** also gave **2g**, together with alkyne **3**.

(4)
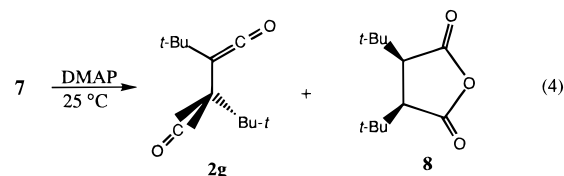
3,4-Di-*tert*-butoxycyclobutenone (**1k**)[14a] was prepared by reaction of silver squarate prepared from 3,4-dihydroxycyclobutenone (squaric acid) with *tert*-butyl chloride (eq 5).


(5)
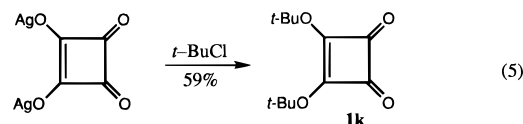
3-Ethoxy-4-(trimethylsilyl)cyclobutenedione (**1o**) was prepared by reaction of the known **9**[12h] with AgOTf/AgOTs. Hydrolysis of **9** using H$_2$SO$_4$ resulted in desilylation, and so this was effected by silver salt induced hydrolysis as shown (eq 6). This latter method has been used in related cases where desilylation is a problem,[4b] and for **9** a 1/1 mixture of salts was found to be most effective.

(6)
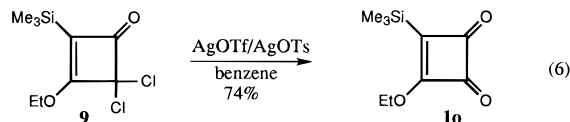
After di-*tert*-butylcyclobutenedione (**1g**) was heated to 180 °C and cooled, no change in the ^{1}H NMR spectrum was detected. Upon photolysis in CDCl$_3$ with 350 nm light, a new ^{1}H NMR signal at δ 1.17 and a new IR band at 2101 cm^{-1} were observed. These were attributed to the bisketene **2g**, with an estimated conversion from **1g** of 5%. Irradiation at lower wavelengths or with benzophenone as a photosensitizer also gave 15% **2g**, along with 35% of the alkyne **3**. Irradiation in C$_6$D$_6$ with 350 nm light gave NMR and IR absorptions attributed to **2g** at δ 1.21 and 2099 cm^{-1}, respectively, and an estimated conversion of 14%.

Photolysis of **1g** in MeOH gave the *d,l*-ester **10**[13b] (eq 7), while photolysis in CDCl$_3$ containing H$_2$O gave the known[3a] *cis*-anhydride **8**. The stereochemical assignment of **10** is based

(7)
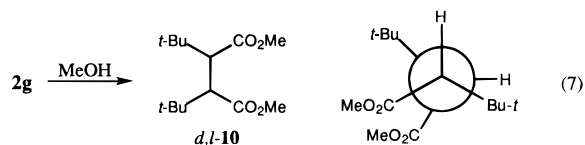
on the vicinal H,H coupling observed from the ^{13}C−H satellites, a technique we have recently used in other studies of succinates.[4d] For *d,l*-**10**, $J_{^{13}C-H}$ = 130.4 Hz and $J_{H,H}$ = 1.2 Hz. The low magnitude of the latter coupling constant is consistent with a near-90° dihedral angle, as expected for the *d,l*-ester.

Laser flash photolyses of cyclobutenediones **1** with time-resolved infrared detection were carried out using a 308 nm laser, either directly or, in the cases of **1f−j** in the presence of 4-methoxyacetophenone as a sensitizer. The appearance of strong infrared bands near 2100 cm^{-1}, assigned to absorption

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Table 1. IR Bands and Rate Constants of Ring Closure of 1,2-Bisketenes **2** Generated from Cyclobutenediones **1**

|	R^1, R^2	ν_1, ν_2 $(cm^{-1})^a$	I_1/I_2	k_{obs} $(s^{-1})^b$	ΣSE^f
a	Ph, H	2103, 2127	0.55	$(1.70 \pm 0.13) \times 10^{-4}$	4.8
b	Ph, Ph	2096, 2110	0.75	$(3.89 \pm 0.15) \times 10^{-2}$	1.8
c	Ph, Me	2093, 2112	0.60	$(3.50 \pm 0.09) \times 10^{-2}$	0.9
d	Ph, CN	2116, 2140	2.68	$(8.51 \pm 1.29) \times 10^{-2}$	1.5
e	Ph, Br	2105, 2132	0.98	0.137 ± 0.022	(-6.8)
f	Me, Me^c	2092, 2114	1.82	$(3.60 \pm 0.09) \times 10^{-2}$	0.0
g	t-Bu, t-Bu^c	2087, 2113	2.63	$(8.19 \pm 0.20) \times 10^{-4}$	0.0
h	Cl, Cl^c	2123, 2154	1.42	$(3.20 \pm 0.80) \times 10^{3}$	-15.4
				$(5.2 \pm 0.5) \times 10^{3\,a}$	
i	Cl, MeO^c	2098, 2142	1.38	$(2.97 \pm 0.90) \times 10^{4}$	-22.2
				$(1.0 \pm 0.1) \times 10^{5\,a}$	
j	t-Bu, i-PrO^c	2092, 2108	1.22	$(3.2 \pm 0.3) \times 10^{4\,a}$	-14.5
k	t-BuO, t-BuO	d		$(2.52 \pm 0.40) \times 10^{4}$	-29.0
l	(t-BuMe$_2$SiC≡C)	2111, 2119	0.60	$(4.23 \pm 0.37) \times 10^{-3}$	1.0
m	(PhC≡C)	d		$(1.59 \pm 0.15) \times 10^{-2}$	1.0
n	PhS, PhS	2112		$(5.62 \pm 0.56) \times 10^{-3}$	0.4
o	Me$_3$Si, EtO	2090, 2104	1.33	$(1.77 \pm 0.14) \times 10^{-3}$	-3.0
p	Me$_3$Si, Ph	2076		$(2.03 \pm 0.20) \times 10^{-6}$	12.4
q	Me$_3$Si, Me	2101		$(4.37 \pm 0.44) \times 10^{-6}$	11.5
r	Me$_3$Si, Me$_3$Si	2084		$(10^{-10})^e$	23.0
s	(CH=CHCH=CH)	2073, 2128	0.81	$(1.9 \pm 0.2) \times 10^{4\,a}$	

^{a} In CH$_3$CN, measured by TRIR. ^{b} In isooctane measured by UV unless noted. ^{c} Generation sensitized with 4-methoxyacetophenone. ^{d} Not measured. ^{e} Estimated, see text. ^{f} Sum of substituent stabilization energies (kcal/mol) defined by eq 9.
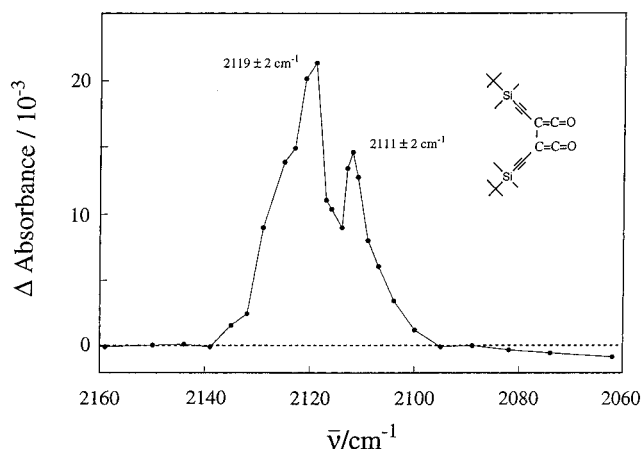
Figure 1. Infared spectrum of (t-BuMe$_2$SiC≡CC=C=O)$_2$ (**2l**) from 308 nm laser flash photolysis of **1l** in CH$_3$CN.

by the ketenyl groups in bisketenes **2**, was observed in most of the examples, as noted in Table 1. Representative spectra, for **2l** (R^1 = R^2 = t-BuMe$_2$SiC≡C) and **2j** (R^1 = t-Bu, R^2 = i-PrO) are shown in Figures 1 and 2, respectively. The bisketenes from **1k,m** were observed only by UV.

Usually two well-resolved ketene bands were observed, and the band positions of each are given, along with the ratios of the maximum peak heights of the two bands (Table 1). *Ab initio* calculations (MP2/6-31G*//MP2/6-31G*)[3d] for **2f** (Me, Me) predict the appearance of IR bands at 2098 and 2113 cm^{-1} (relative intensity (rel int) 1.41), compared to the observed bands at 2092 and 2114 cm^{-1} (rel int 1.82), while HF/6-31G*//HF/6-31G* calculations of **2s** predict IR absorptions at 2062 and 2133 cm^{-1} (rel int 0.96), compared to the observed bands at 2073 and 2128 (rel int 0.81). In the case of **2r** (SiMe$_3$, SiMe$_3$), only a single IR band is observed, at 2084 cm^{-1}. Calculation for (SiH$_3$, SiH$_3$)[3d] predicts absorption bands at 2089 and 2090 cm^{-1}, and these are not resolved experimentally. In the cases of **2n,p–r**, only single bands were observed, but these are also attributed to unresolved doublet absorptions.

In the cases of **2a–g,l,n–r**, the ketenyl infrared bands were long lived on the time scale of the laser flash photolysis
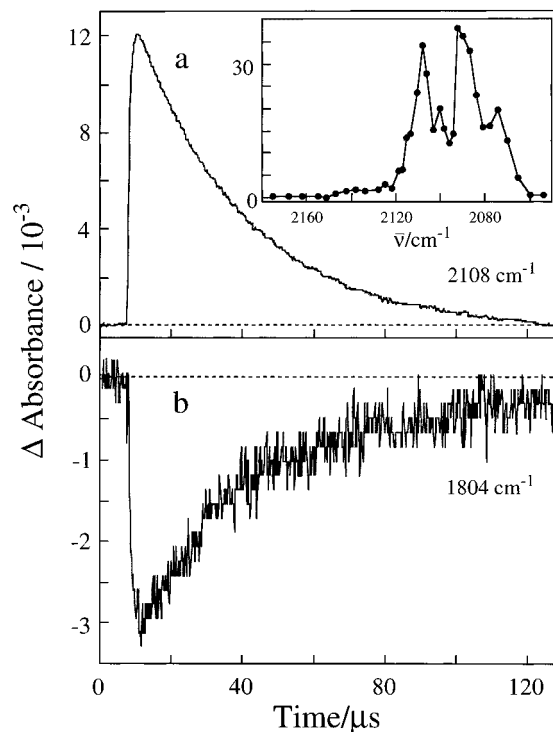
Figure 2. Transient IR absorption traces from 308 nm laser flash photolysis of **1j** in CH$_3$CN with 4-methoxyacetophenone as a sensitizer. (a) Generation and decay of **2j**. The inset shows the transient IR spectrum of **2j**. (b) Bleaching and almost complete recovery of **1j**.

apparatus. For **2a,b,p,q**, the decay of the ketenes was sufficiently slow that these could be generated by conventional UV photolysis, and the kinetics of ring closure were observed by UV spectroscopy.

In the cases of cyclobutenediones **1i,j**, recovery of the original IR absorption after photolysis (monitored at 1804 cm^{-1}) follows the same kinetics as the decay of the corresponding bisketene and is essentially complete (Figure 2). In the case of **1s**, this does not occur, and this bisketene is known[2a] to form dimers. Decarbonylation of the bisketenes may occur upon photolysis,[3a,e] as well as hydration by traces of H$_2$O in the solvent, and these may also contribute to any lack of recovery.

For **1c–g,l–o**, photolyses were carried out by conventional flash photolysis and rate constants for ring closure of the resulting bisketenes were measured using conventional ultraviolet spectroscopy. For **2h,i,k**, the rate constants were obtained using conventional flash photolysis with time-resolved ultraviolet detection in isooctane solvent. For **2h,i**, the rate constants were measured both by TRIR in CH$_3$CN and by UV in isooctane, and those in CH$_3$CN are larger by factors of 1.6 and 3.4, respectively. This is consistent with previous comparisons[3b,4b] in which ring closure rate constants were larger by factors of 1.5–4.3 in the more polar CDCl$_3$ compared to isooctane.

Decarbonylation of the substrates to form the corresponding alkynes was observed with several of the substrates, and this reaction has been previously observed upon photolysis of bisketenes.[3] This was particularly prominent with the bis-(phenylethynyl)-substituted cyclobutenedione **1m**, in which the bisketene was not observed upon laser flash photolysis with IR detection but was seen using lower photolysis power levels with UV detection.

Upon flash photolysis of the bis(t-BuO) cyclobutenedione **1k**,[14a] formation of the bisketene **2k** which reformed **1k** could be observed by UV. Upon continuous photolysis, the cyclopropenone **11**[14b] was formed and isolated (eq 8). The formation of diethoxycyclopropenone has been reported from photolysis

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of **1** (R = R^1 = OEt),[10c] and photolysis of dihydroxycyclobutenedione (**1**, R = R^1 = OH) in an Ar matrix at 10 K led to formation of dihydroxycyclopropenone in a process proposed to involve a ketenylcarbene.[10a] An analogous ketenylcarbene **12** is depicted in eq 8. However, recent calculations[15] at the MP2/6-31G*//MP2/6-31G* level for **1** (R = R^1 = OH) indicate that the thermal conversion of dihydroxycyclobutenedione to the cyclopropenone is a one-step process without the formation of a discrete ketenylcarbene intermediate.


(8)
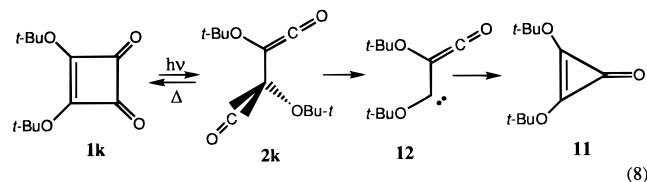
The structure of α,α′-dioxo-*o*-quinonemethide [5,6-bis(ketenylidene)-1,3-cyclohexadiene] (**2s**), benzocyclobutene-3,4-dione (**1s**), and the transition structure (**TSs**) for their interconversion were calculated at the HF/6-31G* level using Gaussian 94,[16a] and energies for this geometry were calculated at the MP2/6-31G* and B3LYP[16b] levels, as reported in Table 2. In previous studies[3c] we have found good agreement between MP2/6-31G*//MP2/6-31G* and MP2/6-31G*//HF/6-31G* energies for similar ring closure reactions of 1,2-bisketenes, and the good agreement between the relative energy changes calculated at the MP2 and B3LYP levels using the HF/6-31G* geometries also indicate that these energies are reliable.

Discussion

The measured rate constants of ring closure of the bisketenes **2** span a range of more than 10^{10}. In addition, a rate constant of 10^{-10} s^{-1} may be estimated for ring closure of the 2,3-(Me$_3$-Si)$_2$ bisketene **2r** from the rate constant of 10^{-6} s^{-1} at 25 °C in CDCl$_3$ for ring opening of **1r** derived from measurements at higher temperatures,[3a] and the equilibrium constant of 3.0 × 10^4 for ring opening of the 3,4-(SiH$_3$)$_2$-substituted cyclobutenedione based on the calculated[3c] ΔG of −6.1 kcal/mol. This extends the range of rates to more than 10^{14}.

These rate constants are affected by the influence of the substituents on both the reactants[11a,b] and the transition states, and as discussed elsewhere,[3c,4b] the latter are influenced by the properties of the product cyclobutenediones.[11c] We have reported[11a,b] calculated stabilization energy (*SE*) parameters for the effect of substituents on ketenes compared to alkenes defined (in kcal/mol) by the isodesmic reaction in eq 9 and have found

$$RCH{=}C{=}O + CH_3CH{=}CH_2 \xrightarrow{\;SE\,=\,\Delta E\;} CH_3CH{=}C{=}O + RCH{=}CH_2 \quad (9)$$
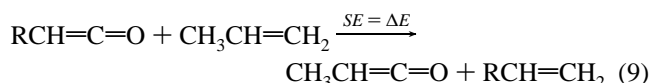
that these can explain many observed properties of ketenes. These give a correlation of the observed rate constants by the relationship log *k*(bisketene) = −(0.29 ± 0.02)Σ*SE* − (2.02 ± 0.26), *r* = 0.96 (Figure 3, Supporting Information). This rather

(15) Sung, K.; Fang, D.; Glenn, D.; Tidwell, T. T. Submitted for publication.

(16) (a) *Gaussian 94*, Revision D2: Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T. A.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Cioslowski, J.; Stefanov, B. B.; Nanayakkara, A.; Challacombe, M.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzales, C.; Pople, J. A. Gaussian, Inc.: Pittsburgh, PA, 1995. (b) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648−5652.

Table 2. *Ab Initio* Calculated Energies (hartrees), Relative Energies (kcal/mol, parentheses), and Geometries of Benzocyclobutenedione (**1s**), 5,6-Bis(oxomethylene)-1,3-cyclohexadiene (**2s**), and Transition State **TSs**

	2s	**TSs**	**1s**
$E_{HF}{}^a$	−454.90102	−454.85494	−454.95880^a
ZPVE	0.09249	0.09062	0.09482
E_{HF} + ZPVE	−454.80853	−454.76432	−454.86398
	(0.0)	(27.7)	(−34.8)
$E_{MP2}{}^b$	−456.24074	−456.22462	−456.30178
E_{MP2} + ZPVE	−456.14825	−456.13400	−456.20696
	(0.0)	(8.9)	(−36.8)
$E_{B3LYP}{}^c$	−457.59952	−457.58072	−457.65243
E_{B3LYP} + ZPVE	−457.50703	−457.49010	−457.55761
	(0.0)	(10.6)	(−31.7)
C$_1$C$_2$	1.493	1.427	1.381
C$_2$C$_3$	1.474	1.434	1.390
C$_3$C$_4$	1.328	1.348	1.379
C$_4$C$_5$	1.469	1.448	1.409
C$_1$C$_7$	1.315	1.375	1.500
C$_1$O	1.147	1.158	1.176
C$_7$C$_8$			1.570
C$_1$C$_2$C$_3$	116.6	119.2	122.4
C$_1$C$_2$C$_8$	122.8	107.1	93.6
C$_2$C$_3$C$_4$	120.2	116.4	115.6
C$_3$C$_4$C$_5$	121.4	122.1	122.0
C$_6$C$_1$C$_7$	133.7	133.7	144.0
C$_1$C$_7$O	177.9	153.7	137.3
C$_7$C$_1$C$_2$C$_8$	35.2	22.4	0.0

^{a} HF/6-31G*//HF/6-31G*. ^{b} MP2/6-31G*//HF/6-31G*. ^{c} B3LYP/6-31G*//HF/6-31G*.

good correlation suggests that the substituent effects on the ketene stabilities have a significant influence on the bisketene reactivity.

The *SE* parameters are correlated with group electronegativities,[17] and electropositive substituents stabilize ketenes.[11a,b] The least reactive bisketenes are those with electropositive Me$_3$-Si groups, while those with electronegative substituents (*e.g.*, *t*-BuO, *t*-BuO; MeO, Cl; Cl, Cl) are the most reactive. The substituents Ph, Me, CN, SH, and HC≡C have rather similar *SE* values, and the substrates bearing only these groups are clustered together on the correlation.

The deviations from the correlation indicate that other factors are involved as well. Thus the 40-fold greater reactivity of the Me, Me compared to the *t*-Bu, *t*-Bu bisketene **2g** reflects the steric crowding in the di-*tert*-butylcyclobutenedione. However, this crowding does not lend steric protection comparable to that found for *t*-Bu$_2$C=C=O, which is indefinitely stable to dimerization.[18] The bisketene **2g** could not be isolated in pure form and appeared sensitive to air, moisture, and further photolysis. The π-donor substituents (RO, PhS, halogen) are expected to stabilize the electron-deficient cyclobutenedione and thus would also be expected to accelerate the ring closure. However, the electronegative character of these groups also destabilizes the ketenyl groups and enhances ring closure, and the respective role of the two effects cannot be separated.

A rapid rate of ring closure of the *o*-quinoketene **2s** would be expected on the basis of the constrained *cisoid* geometry

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Table 3. Calculated Energetics[a] of Ring Closure of Bisketenes **2** to Cyclobutenediones **1**

R, R^1	$E(\mathbf{2})^b$	$E(\mathbf{TS})^b$	$E(\mathbf{1})^b$	log k^c	E_{act}^d	ΔE^d
Me, Me	−381.3533	−381.3237	−381.3772	−1.44	18.6	−15.0
Cl, OH	−837.1304	−837.1134	−837.1696	4.47	10.7	−24.6
Cl, Cl	−1221.1484	−1221.1238	−1221.1727	3.50	15.5	−15.2
SiH$_3$, SiH$_3$[e]	−883.3908	−883.3397	−883.3830	−10.0	32.1	4.9
(CH=CHCH=CH) (**2s**)[f]				4.28	8.9	−36.8

[a] MP2/6-31G*+ZPVE//HF/6-31G*, ref 19. [b] hartrees. [c] Table 1. [d] kcal/mol. [e] Reference 3c. [f] Table 2.

and also because of the benzene resonance gained on ring closure (eq 10). It is, however, surprising that this compound

(10)
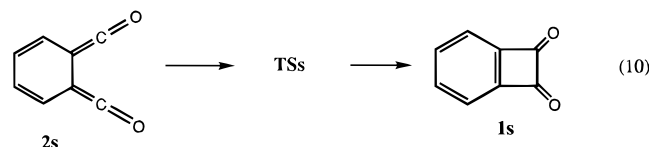
is less reactive than are the acyclic derivatives **2i,k**, and this illustrates the dominant influence of the ketene destabilization by the strongly electronegative substituents on the rate of ring closure in the latter two cases. The calculated geometry of quinoketene **2s** (Table 2) shows a 35.2° dihedral angle between the two ketenyl units, and this non-coplanarity of the ketenyl groups parallels that found in acyclic 1,2-bisketenes (eq 1).[3c,f,4f] This phenomenon has been attributed[3f] to the mutual electronic repulsions at the two electron-rich C$_\beta$ positions of the ketenes and at the two electropositive C$_\alpha$ positions.

In **2s**, the unfavorable electronic interaction between the two C$_\beta$ carbons could be enhanced by antiaromatic effects, as a coplanar structure with excess electron density at the C$_\beta$ carbons would have more than 6π electrons. The six-membered ring in **2s** shows strong bond alternation (Table 2), consistent with a non-delocalized structure.

The ring closure of **2s** to **1s** is calculated to be strongly exothermic, by 31.7−36.8 kcal/mol at the different theoretical levels, but with an appreciable barrier of 8.9 and 10.6 kcal/mol at the MP2 and B3LYP levels, respectively. By contrast, ring closure of **2** (R = R^1 = F)[3c] at the MP2/6-31G*//HF-6-31G* level is calculated to be exothermic by 20.4 kcal/mol, which is 16.4 kcal/mol less than for **2s**, but with a similar barrier of 9.5 kcal/mol compared to that of 8.9 kcal/mol for **2s**.

Even in the transition structure **TSs**, there is a rather large C$_7$C$_1$C$_2$C$_8$ dihedral angle of 22.4° and significant bond alternation in the six-membered ring. The product benzocyclobutenedione **1s** is however fully planar, with greatly reduced bond alternation between the C−C bonds, with a maximum difference of 0.030 Å. These results suggest that there is little gain of aromatic stabilization in the transition structure, leading to the high barrier for ring closure even though the reaction is strongly exothermic.

Calculated barriers for ring closure at the MP2/6-31G* + ZPVE//HF-6-31G* level are available for bisketene **2f** (Me, Me) and **2h** (Cl, Cl),[19] as well as for **2** (R = Cl, R^1 = OH[19] and R = R^1 = SiH$_3$[3c]), which are models for **2i** and **2r**, respectively. These are summarized in Table 3, along with the present results for **2s,** and give the correlation with the experimental rate constants log k(bisketene) = $-(0.67 \pm 0.04)E_{act} + (11.7 \pm 0.05)$, r = 0.98 (Figure 4, Supporting Information). This correlation is comparable to that with the ketene SE parameters (Figure 3, Supporting Information) but also permits the inclusion of **2s**. Overall, the correlation of the theoretical and experimental results is quite satisfactory.

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In summary, a group of 1,2-bisketenes **2** with various combinations of representative substituents have been generated, and the rate constants of their ring closures to the corresponding cyclobutenediones **1** have been correlated with the ketene stabilization parameters SE and with calculated barriers. The 40-fold lower reactivity in ring closure for the 1,2-di-*tert*-butylbisketene (**1g**) compared to the dimethyl analogue **1f** is a measure of the steric crowding in the transition structure for the former.

Experimental Section

Previously reported cyclobutenediones were prepared by the reported methods: **1a**,[1a] **1b**,[1b] **1c**,[12a] **1d**,[12b] **1e**,[12c] **1f**,[12a] **1h**,[12d] **1i**,[12e] **1j**,[12a] **1l**,[12f] **1m**,[12f] **1n**,[12g] **1p**,[3b] **1q**,[3b] **1r**,[3a] and **1s**.[2a]

3-Ethoxy-4-(trimethylsilyl)cyclobut-3-ene-1,2-dione (1o). 4,4-Dichloro-2-(trimethylsilyl)-3-ethoxycyclobutenone (**9**)[12h] (0.55 g, 2.6 mmol) was dissolved in benzene (10 mL), silver trifluoromethanesulfonate (0.67 g, 2.6 mmol) and silver toluenesulfonate (0.73 g, 2.6 mmol) were added in one portion, and the reaction mixture was refluxed for 3 h. The AgCl precipitate was filtered off, the solution was diluted with ether (100 mL) and washed with water, and dried over MgSO$_4$, and the solvent was evaporated. The crude product was purified by TLC (silica gel, 3% EtOAc/hexane) to give **1o** as a yellow oil (0.30 g, 1.52 mmol, 74%): ^{1}H NMR (CDCl$_3$) δ 0.32 (s, 9), 1.49 (t, 3, J = 7.2 Hz), 4.78 (q, 2, J = 7.2 Hz); IR (CDCl$_3$) 1776 (s), 1755 (s), 1557 (s) cm^{-1}; UV $\lambda_{max}^{isooctane}$ 220 (ϵ = 5.4 × 10^4), 255 (ϵ = 4.2 × 10^4 nm); ^{13}C NMR (CDCl$_3$) δ −2.3, 15.6, 70.5, 186.9, 194.9, 197.3, 204.8; EIMS m/z 199 (M$^+$ + 1, 0.5), 183 (M$^+$ − CH$_3$, 1), 170 (M$^+$ − CO, 4.5), 141 (TMSC≡COEt$^+$ − 1, 30), 73 (TMS$^+$, 100); HRMS m/z calcd for C$_8$H$_{11}$O$_3$Si (M$^+$ − CH$_3$) 183.0477, found 183.0480.

3,4-Di-*tert*-butyl-2,4-dichlorocyclobutenone (4). Zinc dust (2.0 g, 0.03 mol) in a 100 mL three-neck flask was heated under N$_2$ with a Bunsen flame for 10 min with stirring. After cooling, di-*tert*-butylacetylene (**3**)[20] in 40 mL of ether was added, followed by dropwise addition with stirring of CCl$_3$COCl (1.4 mL, 0.013 mol) in 15 mL of ether over 1 h at room temperature. The solution was stirred for 16 h and filtered, and the collected solid was washed with 20 mL of ether. The combined filtrate was washed with NaHCO$_3$ and NaCl solutions, dried over MgSO$_4$, and evaporated, and the resulting solid was chromatographed on silica gel (5% EtOAc in hexane) to give **4** (1.9 g, 7.7 mmol, 77%): mp 38.5 °C; ^{1}H NMR (CDCl$_3$) δ 1.08 (s, 9), 1.34 (s, 9); ^{13}C NMR (CDCl$_3$) δ 27.2, 28.6, 35.8, 37.9, 92.8, 128.6, 182.6, 186.8; IR (CDCl$_3$) 1785 (vs), 1568 (s) cm^{-1}; EIMS m/z 248 (89, M$^+$), 199 (100), 141 (52); HRMS m/z calcd for C$_{12}$H$_{18}$Cl$_2$O 250.0580, found 250.0570.

3,4-Di-*tert*-butylcyclobut-3-ene-1,2-dione (1g). To **4** (0.5 g, 2.0 mmol) in 10 mL of benzene was added AgO$_2$CCF$_3$ (0.9 g, 4.1 mmol), and the mixture was refluxed for 6 h. The AgCl precipitate was filtered off, 100 mL of ether was added, and the solution was washed with H$_2$O, dried over MgSO$_4$, and evaporated. The resulting solid was chromatographed on silica gel (3% EtOAc/hexane) to give **1g** (182 mg, 0.94 mmol, 47%) as a yellow solid [mp 57.5−58.0 °C, R_f 0.33 (10% EtOAc/hexane)] and 2-chloro-3,4-di-*tert*-butyl-4-(trifluoroacetoxy)cyclobutenone (**5**) (150 mg, 0.46 mmol, 23%) [R_f 0.44 (10% EtOAc/hexane)]. **1g**: ^{1}H NMR (CDCl$_3$) 1.44 (s, 18); ^{13}C NMR (CDCl$_3$) δ 28.9, 35.4, 198.9, 206.4; IR (CDCl$_3$) 1770 (vs), 1576 (s) cm^{-1}; UV $\lambda_{max}^{isooctane}$ 217 (ϵ = 18 700), 353 (ϵ = 25), 370 (ϵ = 26) nm; EIMS m/z 194 (45, M$^+$), 138 (10), 123 (100), 95 (26), 57 (66); HRMS m/z calcd for C$_{12}$H$_{18}$O$_2$ 194.1307, found 194.1305. **5**: ^{1}H NMR (CDCl$_3$) δ 1.17 (s, 9), 1.37 (s, 9); ^{13}C NMR (CDCl$_3$) δ 26.5, 27.9, 35.4, 36.6, 105.2,

114.0 (q, $J = 285$ Hz), 133.8, 155.8 (q, $J = 42.8$ Hz), 182.1, 183.2; IR (CDCl$_3$) 1798 (vs), 1576 (s) cm^{-1}; EIMS m/z 326 (3), 270 (18), 156 (10), 84 (18), 57 (100); HRMS m/z calcd for C$_{14}$H$_{18}$ClF$_3$O$_3$ 326.0897, found 326.0912.

meso-**2,3-Di-*tert*-butylsuccinyl Chloride (7).** To a suspension of *meso*-**6**[13] (0.1 g, 0.44 mmol) in 20 mL of CH$_2$Cl$_2$ cooled in a dry ice bath was added PCl$_5$ (3 equiv), and the solution was warmed to room temperature over 3 h. The solvent was evaporated, the residue redissolved in 30 mL of ether, and the residual solid removed by filtration. The ether solution was washed five times with H$_2$O (10 mL), dried over MgSO$_4$, and evaporated. The residue was dissolved in hexane, and the mixture was filtered and evaporated to give **7** (93 mg, 35 mmol, 80%): ^{1}H NMR (CDCl$_3$) δ 1.18 (s, 18), 3.27 (s, 2); ^{13}C NMR (CDCl$_3$) δ 29.1, 36.1, 67.2, 174.5; IR (CDCl$_3$) 1801 cm^{-1}; EIMS m/z 251 (2, M$^+$ $-$ CH$_3$), 231 (6), 118 (10), 111 (31), 57 (100); HRMS m/z calcd for C$_{11}$H$_{17}$Cl$_2$O$_2$ 251.0606, found 251.0600.

A solution of **7** (80 mg, 0.30 mmol) in 6 mL of THF with Et$_3$N (61 mg, 0.6 mmol) was heated in a sealed vial for 16 h at 120 °C. The precipitate was removed by filtration and the solvent evaporated. Chromatography on silica gel with elution by 5% EtOAc in hexane gave **1g** (41 mg, 0.21 mmol, 70%).

A solution of **7** (10 mg, 0.04 mmol) in 6 mL of THF with DMAP (10 mg, 0.08 mmol) was stirred for 3 h at room temperature. The solvent was evaporated, and the residue was dissolved in CDCl$_3$. The presence of bisketene **2g** was indicated by the ^{1}H NMR absorption at δ 1.17 and by the IR absorption at 2101 cm^{-1}, and the presence of **8** was indicated by the ^{1}H NMR absorptions at δ 1.05 and 2.60.

Dimethyl *d,l*-2,3-Di-*tert*-butylsuccinate (*dl*-10).[13b] Dione **1g** (52.0 mg, 0.268 mmol) in 0.5 mL of CDCl$_3$ and 50 μL of MeOH was irradiated for 12 h at 6 °C with 350 nm light. The solvent was evaporated, leaving *d,l*-**10** (69.2 mg, 0.268 mmol, 100%) as the sole product: ^{1}H NMR (CDCl$_3$) δ 1.02 (s, 18), 2.50 (s, 2), 3.63 (s, 6); ^{13}C NMR (CDCl$_3$) δ 28.0, 34.3, 51.1, 54.0, 174.2; IR (CDCl$_3$) 1733 (vs), 1721 (vs) cm^{-1}; EIMS m/z 227 (M$^+$ $-$ MeO, 14), 145 (90), 131 (58), 113 (65), 57 (*t*-Bu$^+$, 100). The stereochemistry was confirmed by the ^{13}C satellites of the ^{1}H signal at δ 2.50: $J_{^{13}C-H} = 130.4$ Hz, $J_{H,H} = 1.2$ Hz.

Photolysis of **1g** (28.0 mg, 0.144 mmol) in 0.5 mL of CDCl$_3$ containing 20 μL of H$_2$O with 350 nm light for 20 h at 5 °C followed by evaporation of the solvent and recrystallization from THF/hexane gave the anhydride (*Z*)-**8**[3a] (24.2 mg, 0.114 mmol, 79%): ^{1}H NMR (CDCl$_3$) δ 1.05 (s, 18), 2.60 (s, 2).

Di-*tert*-butyl Squarate (1k).[14a,c] Squaric acid (2.73 g, 0.024 mol) in 125 mL of water was neutralized with 1 N NaOH, then AgNO$_3$ (8.2 g, 0.048 mol) in 100 mL of H$_2$O was added, and the mixture was stirred for 10 min. The light yellow precipitate was filtered, washed with H$_2$O, acetone, and ether, and dried to give 6.0 g of silver squarate. The dried salt (5.0 g, 0.015 mol) was stirred for 18 h with *t*-BuCl (30 mL) in 50 mL of dry ether at 25 °C. The precipitated AgCl was removed by filtration through anhydrous K$_2$CO$_3$. The solvent was evaporated, and the solid product was chromatographed on silica gel (5% EtOAc in hexane) to give **1k**[14a,c] (2.0 g, 8.8 mmol, 59%) as colorless crystals: ^{1}H NMR (CDCl$_3$) δ 1.61, UV λ_{max}^{hexane} 250, 339 nm.

Di-*tert*-butoxycyclopropenone (11).[14b] A solution of **1k** (100 mg, 0.44 mmol) in 50 mL of ether in a quartz tube was photolyzed for 18 h with 254 nm light. The ^{1}H NMR spectrum indicated the presence of **11** (92%) with 2% residual **1k**. Chromatography on silica gel (5% EtOAc in hexane) gave **11**[14b] (22.0 mg, 0.11 mmol, 25%): ^{1}H NMR (CDCl$_3$) δ 1.47; ^{13}C NMR (CDCl$_3$) δ 28.5, 84.3, 127.2, 137.2; UV $\lambda^{pentane}$ 230 nm (sh, $\epsilon = 1200$), 290 nm, (sh, $\epsilon = 100$).

Kinetics. Photolyses of **1c**−**g,l**−**o** were carried out using a conventional flash photolysis apparatus, and the change in UV absorption with time at a wavelength of maximum change was monitored with a Cary 220 instrument. Photolysis of **1h**−**k** was done using conventional flash photolysis with time-resolved UV detection. Several separate solutions were prepared for each compound, and multiple kinetic runs were carried out for each solution.

For kinetic determinations on **2a,b** 10^{-2} M solutions of **1a** (CH$_3$-CN) or **1b** (in pentane) were irradiated for 5 min at -80 °C with 350 nm light. Aliquots (3−10 μL) of these solutions were added to 1.2 mL of solvent in the UV cell, and the change in absorbance with time was monitored [for **2a** increase at 280 (isooctane) or 287 nm (CDCl$_3$) and decrease at 240 (isooctane) or 260 nm (CDCl$_3$); for **2b** decrease at 240 and increase at 320 nm].

Laser flash photolyses with time-resolved IR detection were carried out using a 308 nm Lumonics Excimer-500 laser and a Mutek MPS-1000 diode laser as a monitoring source. Details of the system are provided elsewhere.[5a]

Supporting Information Available: ^{1}H NMR spectra and Figures 3 and 4 (9 pages). See any current masthead page for ordering and Internet access instructions.

JA9722685