

Structural Effects on Interconversion of Oxygen-Substituted Bisketenes and Cyclobutenediones

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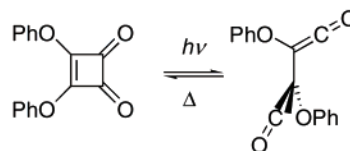
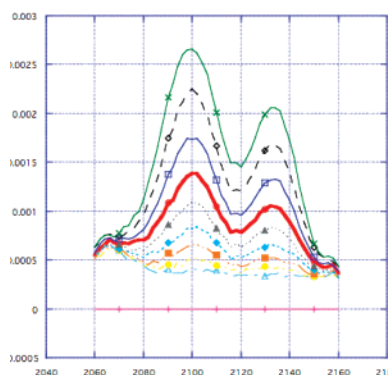
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Cyclobutenediones **5** disubstituted with HO (**a**), MeO (**b**), EtO (**c**), *i*-PrO (**d**), *t*-BuO (**e**), PhO (**f**), 4-MeOC₆H₄O (**g**), 4-O₂NC₆H₄O (**h**), and 3,4-bridging OCH₂CH₂O (**i**) substituents upon laser flash photolysis gave the corresponding bisketenes **6a–i**, as detected by their distinctive doublet IR absorptions between 2075 and 2106 and 2116 and 2140 cm^{−1}. The reactivities in ring closure back to the cyclobutenediones were greatest for the group **6b–e**, with the highest rate constant of $2.95 \times 10^7 \text{ s}^{-1}$ at 25 °C for **6e** (RO = *t*-BuO) in isooctane, were less for **6a** (RO = OH, $k = 2.57 \times 10^6 \text{ s}^{-1}$ in CH₃CN), while **6f–i** were the least reactive, with the lowest rate constant of $3.8 \times 10^4 \text{ s}^{-1}$ in CH₃CN for **6h** (RO = 4-O₂NC₆H₄O). The significantly reduced rate constants for **6f–i** are attributed to diminution of the electron-donating ability of oxygen to the cyclobutenediones **5f–h** by the ArO substituents compared to alkoxy groups and to angle strain in the bridged product cyclobutenedione **5i**. The reactivities of the ArO-substituted bisketenes **6f–h** in CH₃CN varied by a factor of 50 and gave an excellent correlation of the observed rate constants log *k* with the σ_p constants of the aryl substituents. Computational studies at the B3LYP/6-31G(d) level of ring-closure barriers are consistent with the measured reactivities. Photolysis of squaric acid (**5a**) in solution provides a convenient preparation of deltic acid (**7**).

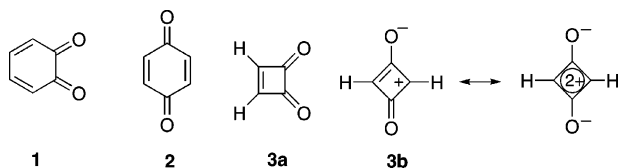
Introduction

Evidence for the instability of oxygen-substituted ketenes was obtained as long ago as 1911, when efforts to prepare MeOCPh=C=O as an isolable compound were unsuccessful.^{1a} Extensive further investigations have confirmed the

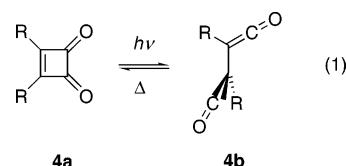
high reactivity of these species, which have only been observed in a few cases in inert matrices^{1b–e} or using fast reaction techniques^{1f–h} by their distinctive ketenyl IR absorption. Nevertheless, such ketenes have found extensive applications in synthesis, including those with MeO, EtO, BnO, *t*-BuO, PhO, MsO, Me₃SiO, AcO, and HO substituents.^{1i–l} Usually, these reactions involve generation and in situ capture of the ketenes.

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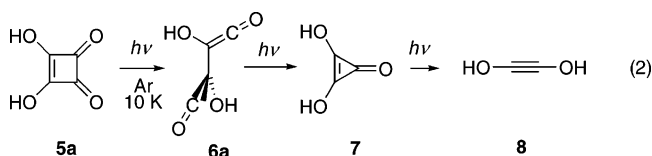
Cyclobutenediones are sources of observable bisketenes and are the first examples of the family of fully conjugated cyclic enediones, of which the 1,2- and 1,4-benzoquinones **1** and **2** are the most familiar representatives. The parent 1,2-cyclobutenedione (**3a**)^{2a–f} has long attracted interest for theoretical reasons, and substituted cyclobutenediones are valuable in synthesis.^{2g–k} The parent 1,3-isomer (**3b**), for which no Kekulé structure without formal charges may be drawn, is unknown, but substituted derivatives, known as 1,3-squaraines, have many practical applications.³



Upon photolysis, 1,2-cyclobutenediones **4a** form 1,2-bisketenes **4b** (eq 1), which have twisted almost perpendicular conformations as shown.^{1j,4} The stabilities of bisketenes **4b** relative to cyclobutenediones **4a** cover a vast range, and bisketenes **4b** with two electropositive trialkylsilyl substituents have been found to be more stable than cyclobutenediones **4a**, but in all other known cases, the latter are preferred.⁴ Rate



1,2-Dihydroxycyclobutenedione **5a** (squaric acid)^{5a,b} upon photolysis in a matrix at 10 K formed bisketene **6a**, as identified by the IR absorption at 2125 cm⁻¹, and with further photolysis at 10 K successively forms deltic acid **7** and dihydroxyacetylene **8** (eq 2).^{5c} Other reported photolyses of di(oxygen)-substituted cyclobutenediones include those with di(EtO),^{6a–c} di(*i*-PrO),^{6d} di(*t*-BuO),^{4c,6d} di(Me₃SiO),^{6c} and di(AcO)^{6e,f} substituents. Cyclopropanones and alkynes are observed products in some of these reactions,^{6a–d} as in eq 2, and these have been proposed to form through further reactions of unobserved bisketene intermediates.^{6a,d,e}



The goal of the present investigation was to characterize examples of oxygen-substituted 1,2-bisketenes in solution and to obtain quantitative measurements of their reactivity and stability. The results would increase the understanding of the properties of oxygen-substituted ketenes and bisketenes and facilitate their practical application.

Results

Squaric acid (**5a**) is commercially available, and cyclobutenediones **5b–e**, RO = MeO,^{7a} EtO,^{6a,g} *i*-PrO,^{6d} and *t*-BuO,^{6d} are known compounds. The *i*-PrO compound **5d** was prepared by

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RO	method, solvent	ν_1, ν_2 (cm^{-1})	k (s^{-1})	$k(\text{CH}_3\text{CN})/$ $k(\text{isooctane})$
HO (6a)	UV, ^a CH ₃ CN		$(2.57 \pm 0.20) \times 10^6$	
MeO (6b)	IR, isooctane	2084, 2122	$(1.26 \pm 0.02) \times 10^7$	
EtO (6c)	IR, isooctane	2082, 2118	$(1.46 \pm 0.08) \times 10^7$	
<i>i</i> -PrO (6d)	IR, isooctane	2078, 2116	$(1.84 \pm 0.09) \times 10^7$	
<i>t</i> -BuO (6e)	IR, isooctane	2075, 2122	$(2.95 \pm 0.08) \times 10^7$ ^h	
PhO (6f)	UV, ^b CH ₃ CN		$(5.66 \pm 0.28) \times 10^5$	
	IR, CH ₃ CN	2100, 2134	$(6.68 \pm 0.18) \times 10^5$	
	IR, ^g CH ₃ CN	1750, 1824	$(7.24 \pm 0.11) \times 10^5$	
	CH ₃ CN		6.31×10^5 (ave) ⁱ	2.4
	UV, ^c isooctane		$(2.62 \pm 0.05) \times 10^5$	
4-MeOC ₆ H ₄ O (6g)	UV, ^d CH ₃ CN		$(1.60 \pm 0.04) \times 10^6$	
	IR, CH ₃ CN	2092, 2126	$(1.80 \pm 0.03) \times 10^6$	
	IR, ^g CH ₃ CN	1748, 1810	$(2.52 \pm 0.34) \times 10^6$	
	CH ₃ CN		1.88×10^6 (ave) ^j	2.5
	UV, ^d isooctane		$(7.42 \pm 0.50) \times 10^5$	
4-O ₂ NC ₆ H ₄ O (6h)	UV, ^e CH ₃ CN		$(3.22 \pm 0.04) \times 10^4$	
	IR, CH ₃ CN	2106, 2140	$(4.02 \pm 0.01) \times 10^4$	
	IR, ^g CH ₃ CN	1818, 1754	$(4.61 \pm 0.40) \times 10^4$	
	CH ₃ CN		3.77×10^4 (ave) ^j	
OCH ₂ CH ₂ O (6i)	UV, ^f CH ₃ CN		$(1.65 \pm 0.10) \times 10^5$	
	IR, CH ₃ CN	2096, 2124	$(1.98 \pm 0.10) \times 10^5$	
	IR, ^g CH ₃ CN	1822, 1744	$(2.28 \pm 0.22) \times 10^5$	
	CH ₃ CN		1.89×10^5 (ave) ^j	6.4
	UV, ⁱ isooctane		$(2.94 \pm 0.04) \times 10^4$	

1770 *J. Org. Chem.*, Vol. 73, No. 5, 2008

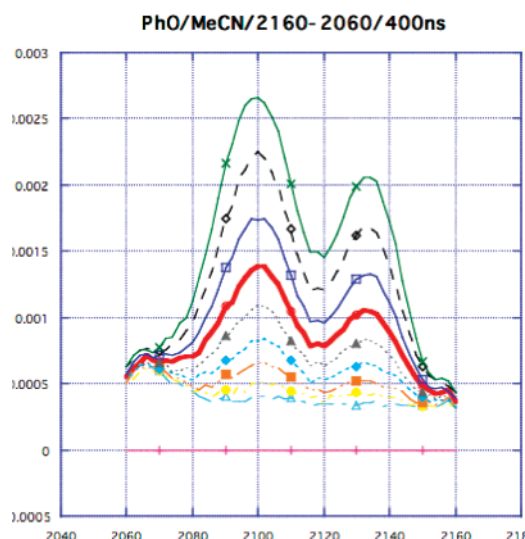
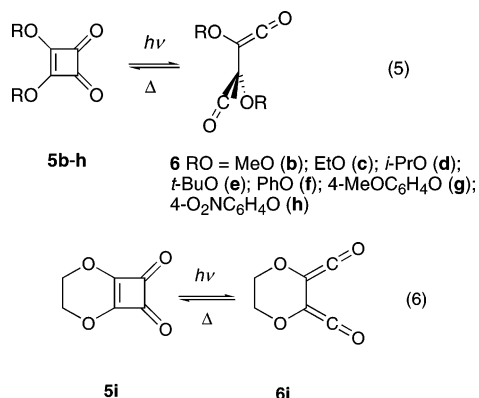


FIGURE 1. IR absorption and decay of bisketene **6f** (RO = PhO) in CH_3CN forming cyclobutenedione **5f** (X axis cm^{-1} , Y axis OD).

signal between 2116 and 2140 cm^{-1} (Table 1). The ketenyl IR absorption for **6f** in CH_3CN is shown (Figure 1), and similar absorptions in isooctane or CH_3CN are shown for the other bisketenes in the Supporting Information. These absorptions for **6b–e** in isooctane decayed with good first-order kinetics, with rate constants between $(1.26 \text{ to } 2.95) \times 10^7 \text{ s}^{-1}$ (Table 1). However, in CH_3CN , the ketenes **6b–e** were apparently too short-lived for observation with our IR apparatus, but the longer-lived bisketenes **6f–i** were observed and rate constants for ring closure measured in isooctane and/or CH_3CN (Table 1). Previously, CH_3CN solvent was shown to give bisketene lifetimes 1.6–3.4 times less than in isooctane,^{4c} and for **6f–i**, the differences are 2.4–6.4. However, **6f–i** had significantly lower reactivity in ring closure in isooctane than did **6b–e**, with a range in rate constants of $(0.29 \text{ to } 7.42) \times 10^5 \text{ s}^{-1}$, compared to $(1.26 \text{ to } 2.95) \times 10^7 \text{ s}^{-1}$ for the latter (Table 1). Rate constants for the growth of the IR absorptions of the aryloxycyclobutenediones **5f–h** were also measured (Table 1 and Supporting Information) and were in agreement with the rate constants for decay of the corresponding bisketenes.



The tethered oxygen-substituted bisketene **6i** was generated by laser flash photolysis of **5i** in acetonitrile or isooctane (eq 6). The ketene was characterized by IR bands at 2096 and 2124 cm^{-1} in CH_3CN (Figure 2), and the decay of this absorption

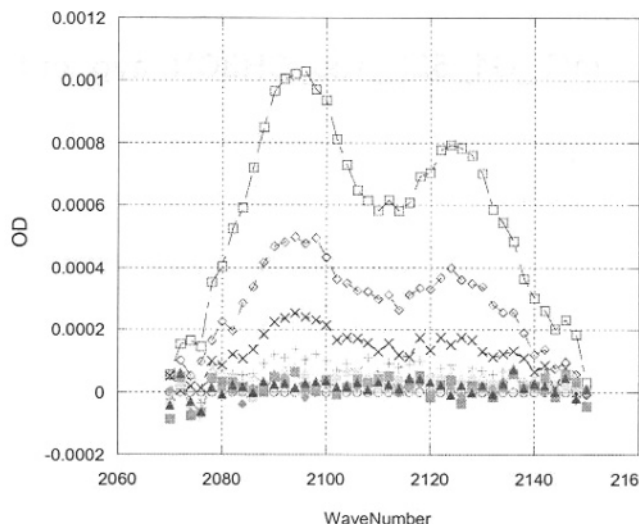


FIGURE 2. IR absorption and decay (4 μs intervals between curves) of bisketene **6i** in CH_3CN forming cyclobutenedione **5i**.

and the concomitant growth of the diketone absorption at 1744 and 1822 cm^{-1} were monitored, with rate constants given in Table 1.

Computations at the B3LYP/6-31G(d) level were made using Gaussian 98¹⁰ of the structures and energies of cyclobutenediones **5a** (RO = HO), **5b** (RO = MeO), **5e** (RO = *t*-BuO), and for the bridged substrate **5i**, the transition states **9** for ring opening of the cyclobutenediones **5**, and the corresponding bisketenes **6** (Table 2). The calculated geometries are given in Tables S-4 and S-5 (Supporting Information).

Discussion

The rate constants for ring closure of the alkoxy-substituted bisketenes **6b–e** in isooctane rank with the largest which have been observed; for comparison, the largest rate constant that has previously been reported for bisketene ring closure is for **4b** (R = Me₂N) of $9.58 \times 10^7 \text{ s}^{-1}$ in CH_3CN .^{4a} Direct comparison of the rate constants is not possible, as those for **6b–e** were measured in isooctane. Rate constant ratios $k(\text{CH}_3\text{CN})/k(\text{isooctane})$ averaging 13 have been measured for R₂N-substituted bisketenes (16 and 9.4),^{4a} while those for RO-substituted ketenes measured here have an average value of 3.8. Whichever value is used for comparison, bisketenes **6b–e** are indicated to be among the most reactive ever studied. The high reactivity of **6b–e** may be attributed to the high electronegativity of these substituents, which has been correlated with decreased ketene stability.^{4d,e} The rate constant for **6a** (RO = HO) in CH_3CN is less than that for **6b** (RO = MeO) in isooctane by a factor of 5.0, and assuming the $k(\text{CH}_3\text{CN})/k(\text{isooctane})$ rate

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TABLE 2. B3LYP/6-31G(d) Calculated Energies for Cyclobutenediones **5**, Ring-Opening Transition States **9**, and Bisketenes **6** (Hartrees), and Relative Energies (kcal/mol)

RO	reactant 5	<i>E</i> (rel)	TS 9	<i>E</i> (rel)	bisketene 6	<i>E</i> (rel)	ΔE^a
HO (a)	−454.45102	0.00	−454.38403	42.04	−454.39609	34.47	7.56
MeO (b)	−533.06493	0.00	−533.00084	40.22	−533.01265	32.81	7.41
<i>t</i> -BuO (e)	−768.97697	0.00	−768.90709	43.85	−768.91618	38.14	5.71
PhO (f)	−916.54387	0.00	−916.48539	36.70	−916.49996	27.55	9.15
(OCH ₂) ₂ (i)	−531.85254	0.00	−531.78307	43.60	−531.80772	28.13	15.47

^a Ring closure barrier, kcal/mol.**TABLE 3.** Substituent Constants for Substituted Oxygen and Nitrogen Groups¹¹

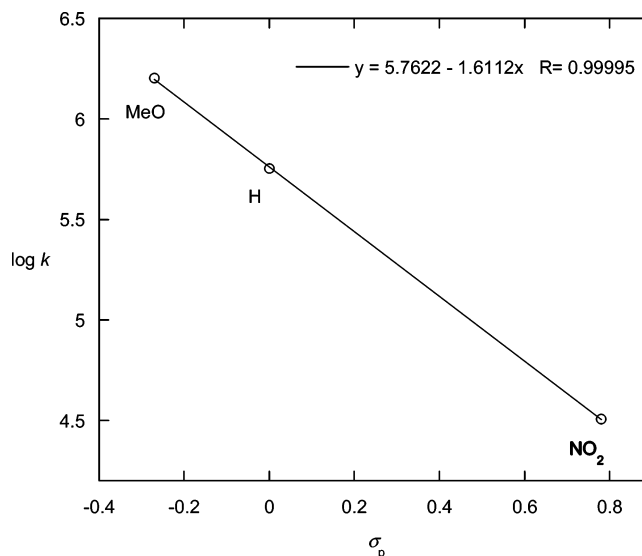
RO	σ_p^+	σ_p	RR ¹ N	σ_p^+
HO	−0.92	−0.36	H ₂ N	−1.30
MeO	−0.78	−0.27	MeNH	−1.81
EtO	−0.81		Me ₂ N	−1.70
<i>i</i> -PrO	−0.85		PhNH	−1.40
PhO	−0.50			

ratios of 3–12 apply for **6a**, then this bisketene is less reactive than is **6b** by a considerably larger factor.

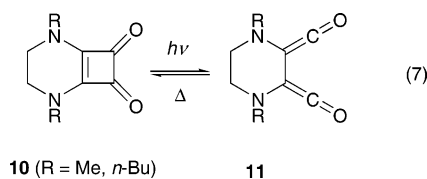
For the alkoxy substituents, the rate constants in isooctane $k_{\text{obs}} = (1.26, 1.46, 1.84, \text{ and } 2.95) \times 10^7 \text{ s}^{-1}$ for RO = MeO, EtO, *i*-PrO, and *t*-BuO, respectively, at 25 °C, are rather similar, with a small but steady increase with increasing alkyl group size. The increase is consistent with available σ_p or σ_p^+ substituent constants (Table 3)¹¹ and suggests the rate increases are due to increased conjugative electron donation stabilizing the forming cyclobutenedione products. The rate constant for **6f** (RO = PhO) is significantly less than these, by factors of 48–110, and this is also consistent with the significantly reduced electron donor ability of this group as measured by the σ_p^+ value of −0.50. The rate constants of **6f–h** (RO = PhO, 4-MeOC₆H₄O, and 4-O₂NC₆H₄O, respectively, by UV in CH₃CN) differ by a factor of 50 and give a correlation (Figure 3) of log *k* with σ_p parameters for the aryl substituents with a slope $\rho = -1.61$ ($r = 1.000$). The correlation with σ_p^+ parameters was not as good ($r = 0.97$). The faster rates of ring closure with electron-donating aryl substituents are also consistent with stabilization of the forming electron-deficient cyclobutenedione groups by the ring substituents on ArO.

The lower reactivity of **6a** (RO = HO) in closure to the cyclobutenediones **5a** compared to the alkoxy analogues **6b–e** is an exception to the trend for greater reactivity for bisketenes **6** with greater magnitude of the substituent σ_p^+ value. However, the calculated barriers for the reaction (Table 2) are in qualitative agreement with the observed trend for ring closure of **6**: *t*-BuO > MeO > HO > PhO > (OCH₂)₂. This could arise from an unexpected stabilization of the bisketene or destabilization of the cyclobutenedione.

The rate constant of $2.94 \times 10^4 \text{ s}^{-1}$ for ring closure of the oxygen-substituted and tethered bisketene **6i** in isooctane to the cyclobutenedione **5i** (eq 6) is much less than that for the acyclic alkoxy-substituted analogues **6b–e**, by a factors of 4×10^2 to 10^3 , but is greater than those of the amine-substituted analogues **11** (R = Me) forming cyclobutenediones **10** (eq 7) by factors of 5.0 (R = Me) and 2.9 (R = *n*-Bu).^{4a} The rate reduction in ring-closure reactivity for the tethered amino substituents compared to the open chain derivatives was attributed to the

**FIGURE 3.** Correlation of log *k* with σ_p for reactivity of bisketenes **6** (RO = R¹C₆H₄O; R¹ = MeO, H, NO₂).

ring strain induced upon cyclization, which forms a four-membered ring fused to a six-membered ring.^{4a} The relative unreactivity of **6i** is evidently due to the same cause, and the greater reactivity of **6i** compared to **11** is consistent with the results for acyclic substituents and is attributable to greater destabilization of the ketenyl groups and stabilization of the cyclobutenedione by the oxygen substituents.



In summary, oxygen-substituted bisketenes **6b–i** have been generated and observed by IR in solution. The reactivities of the bisketenes in ring closure have been measured, and those for alkoxy substituents rank with the greatest which have been reported, a result attributable to the strong electron donor power and ketene destabilizing ability of these substituents. By contrast, aryloxy-substituted bisketenes are significantly less reactive, as expected for the diminished electron donor ability of these groups. The tethered bisketene **6i** is also relatively unreactive, a result attributed to ring strain in the corresponding cyclobutenedione. Photolysis of squaric acid (**5a**) in solution provides a convenient preparation of deltic acid (**7**).

Experimental Section

Cyclobutenedione **5d** (RO = *i*-PrO)^{6d} was prepared from the reaction of squaric acid (**5a**) with isopropanol and acid and was

(11) Hansch, C.; Leo, A.; Taft, R. W. *Chem. Rev.* **1991**, *91*, 165–195.

converted to **5b** (RO = MeO)^{6a} by reaction with methanol. The EtO (**5c**),^{6g} *t*-BuO (**5e**),^{6d} and PhO (**5f**)^{7b} derivatives were prepared by the reported procedures. Aryloxy cyclobutenediones **5g,h** were prepared as for **5f**. Cyclobutenediones **5f** (RO = PhO), **5g** (RO = 4-MeOC₆H₄O), **5h** (RO = 4-O₂NC₆H₄O), and **5i** have been reported,^{7b,c} but no specific experimental details or characterization were given.

3,4-(1',4'-Dioxatetramethylene)cyclobut-3-ene-1,2-dione (5i).^{7c} To a solution of squaric acid (114 mg, 1.00 mmol) and anhydrous ethylene glycol (55.8 μ L, 62 mg, 1.00 mmol) in dry benzene (20 mL) was added 1 drop of concd H₂SO₄, and the mixture was refluxed overnight and then concentrated under reduced pressure. The residue was purified by flash chromatography (silica gel, EtOAc/hexanes 2:1 v/v) to give the squarate **5i** (20 mg, 14%) as a white solid: mp 112–114 °C; ¹H NMR (300 MHz, CDCl₃) δ 4.61 (s, 4H); ¹³C NMR (100 MHz, CDCl₃) δ 186.1, 186.0, 68.1; EIMS (*m/z*) 140 (*M*⁺), 112, 56; HREIMS *m/z* calcd for C₆H₄O₄ 140.0110, found 140.0116; IR (KBr) 1822, 1744, 1729, 1616 cm⁻¹; UV/vis (CH₃CN) (λ_{max} , ϵ) 243 nm (1.81 $\times$ 10⁴).

Deltic Acid (7). Squaric acid (**5a**, 222 mg, 1.95 mmol) was dissolved in H₂O (50 mL) and then diluted with CH₃CN (400 mL) in a quartz tube (4.5 cm diameter, height 28 cm) and irradiated for 24 h using 254 nm light. The solvent was evaporated under vacuum to give a yellow solid which was washed several times with CH₃CN to give **7** as a white solid (84 mg, 50%): mp 213–215 °C (decomp) (lit^{6b} decomp 180 °C); ¹³C NMR (100 MHz, DMSO-*d*₆) δ 168.4; ¹³C NMR (100 MHz, CD₃OD) δ 132.3; IR (KBr) 3421, 2297, 2339, 2362, 2271, 1979, 1934, 1617, 1466, 1411, 1025, 965,

911, 418 cm⁻¹; EIMS *m/z* 104 ([*M* + H₂O]⁺, 16), 87 ([*M* + H]⁺, 38), 68 ([*M* – H₂O]⁺, 100); HRESIMS *m/z* calcd for C₃H₃O₃ ([*M* + H]⁺) 87.0082, found 87.0080.

Kinetic Measurements. Kinetic measurements by IR spectroscopy of the re-formation of cyclobutenediones **5** from bisketenes **6** (RO = MeO (**b**), EtO (**c**), *i*-PrO (**d**), *t*-BuO (**e**), PhO (**f**), 4-MeOC₆H₄O (**g**), 4-O₂NC₆H₄O (**h**), and OCH₂CH₂O (**i**)) were measured at Kyushu University with ketene generation using a Nd:YAG laser (266 nm) and 1.0 $\times$ 10⁻³ M solutions with observations by IR. Kinetic measurements using UV spectroscopy were done at the University of Toronto as previously reported,^{4a-c} by photolysis with an excimer laser (KrF, 248 nm), or Nd:YAG laser (266 nm) to generate the unobserved transient bisketenes, with depletion of the cyclobutenedione and observation of the re-formation of the cyclobutenedione absorption by UV.

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Supporting Information Available: Experimental and computational details. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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