Kinetic and Theoretical Studies of Ring Closure of Unstabilized Bisketenes to Cyclobutenediones[1]

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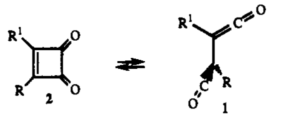
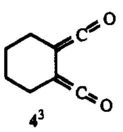
The interconversions of monophenyl and diphenyl 1,2-bis(ketenes) **1a**[2a] and **1b**[2b] with the corresponding cyclobutenediones **2** were first reported in 1961.[2] Subsequent studies of this family have included bisketenes **1c–e**, **3**, and **4**, and in a few cases the bisketenes were detected by infrared (IR) spectroscopy at low temperatures.[3–5] However, none of these bisketenes have been observed by NMR, no measurements of their rates of conversion to the more stable cyclobutenediones have been reported, and there have been no interpretations offered of the factors governing their reactivities in re-formation of the cyclobutenediones.

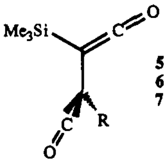


1a (R = Ph, R^1 = H)[2a,8]
1b (R = R^1 = Ph)[2b,3a-d]
1c (R = R^1 = Me)[3c,8]
1d (R = OH, R^1 = H)[3e]
1e (R = R^1 = H)[5]

We have recently studied the trimethylsilyl-substituted buta-1,3-diene-1,4-diones **5–7** generated by photochemical and thermal ring opening of the corresponding cyclobut-3-ene-1,2-diones **2**. Bisketene **5** (R = Me_3Si) is thermodynamically stable relative to **2**,[6a,b] while bisketenes **6** and **7** can be generated and observed at room temperature, but the corresponding cyclobutenediones **2** are more stable and are re-formed from **6** and **7** at elevated temperatures.[6c,d] 1,2-Bis(ketenes) are found by photoelectron and dipole moment measurements,[6f] and by calculation,[6e,f] to favor the twisted almost perpendicular conformations shown.



4[3]

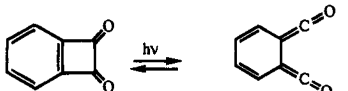


5 R = Me_3Si
6 R = Ph
7 R = Me

We have now applied the method of laser flash photolysis (LFP) generation of nonstabilized bisketenes from cyclobutenediones with their detection by time-resolved infrared spectroscopy (TRIR), which is well suited for studies of ketenes because of their distinctive IR bands near 2100 cm^{-1}.[7] The results are given in Table 1 along with new results for **1a** and **1b** and previous data on **6** and **7**.[6c]

Bisketenes **1a–c**, **3**, and **8–11** generated by LFP-TRIR all show two IR bands near 2100 cm^{-1} (Table 1), and as suggested for **3**[4c] these are assigned to a coupled vibration of the two ketenyl groupings. The generation of **8–11** has not been reported previously and was achieved by the photolysis of the appropriate cyclobutenediones,[8] which either are known[8a,c,d] or are prepared[6a,b] from the corresponding 4,4-dichlorocyclobut-2-enones.[8b] High-level *ab initio* calculations[9] of **1c** give good agreement with the observed band positions and their relative intensities (Table 1). Experimentally[6b] only a single IR band at 2084 cm^{-1} was observed for the persistent bis(trimethylsilyl) bisketene **5**, and although the calculations predict two bands at 2089 and 2090 cm^{-1} for the bis(SiH_3)-substituted compound, these are close together and to the predicted position, so this result is also in good agreement with experiment.

Bisketene **3** has been pursued by several groups,[4] and we report the first kinetics of ring closure of **3** to benzocyclobutadienedione **12**, measured in CH_3CN by TRIR, both by measuring the decay of the absorption of **3** at 2128 cm^{-1} (k_{obs} = 1.9 × 10^4 s^{-1}) and by measuring the rate of re-formation of **12** at 1781 cm^{-1} (k_{obs} = 1.8 × 10^4 s^{-1}). The recovery of the signal of **12** was not complete (Figure 1), indicating that some loss of starting material had occurred.



12 **3** (1)

Recent *ab initio* calculations in this laboratory have predicted that bisketenes that are thermodynamically unstable relative to the corresponding cyclobutenediones nevertheless have appreciable kinetic barriers to ring closure.[6e] We calculate that, at the MP2/6-31G*//MP2/6-31G* *ab initio* level, **3** is 38.2 kcal/mol less stable than **12**, with a dihedral angle of 34.2° between the exocyclic ketenyl groups. The appreciable lifetime of **3** at room temperature (Figure 1) shows that, even in this case, with a strong thermodynamic driving force and a geometry fixed in a suitable orientation, there is still a barrier to ring closure. We

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(2) (a) Mallory, F. B.; Roberts, J. D. *J. Am. Chem. Soc.* **1961**, *83*, 393–397. (b) Blomquist, A. T.; LaLancette, E. A. *J. Am. Chem. Soc.* **1961**, *83*, 1387–1391.

(3) (a) Obata, N.; Takizawa, T. *J. Chem. Soc., Chem. Commun.* **1971**, 587–588. (b) Obata, N.; Takizawa, T. *Bull. Chem. Soc. Jpn.* **1977**, *50*, 2017–2020. (c) Chapman, L.; McIntosh, C. L.; Barber, L. L. *J. Chem. Soc., Chem. Commun.* **1971**, 1162–1163. (d) Bird, C. W. *Chem. Commun.* **1968**, 1537. (e) Hochstrasser, R.; Wirz, J. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 181–183. (f) Diederich, F.; Rubin, Y. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1101–1123. (g) Miller, R. D.; Kirchmeyer, S. *J. Org. Chem.* **1993**, *58*, 90–94.

(4) (a) Staab, H. A.; Ipaktschi, J. *Chem. Ber.* **1968**, *101*, 1457–1472. (b) Boate, D. R.; Johnston, L. J.; Kwong, P. C.; Lee-Ruff, E.; Scaiano, J. C. *J. Am. Chem. Soc.* **1990**, *112*, 8858–8863. (c) Mosandl, T.; Wentrup, C. *J. Org. Chem.* **1993**, *58*, 747–749. (d) Chapman, O. L.; Mattes, K.; McIntosh, C. L.; Pacansky, J.; Calder, G. V.; Orr, G. *J. Am. Chem. Soc.* **1973**, *95*, 6134–6135. (e) Simon, J. G. G.; Münzel, N.; Schweig, A. *Chem. Phys. Lett.* **1990**, *170*, 187–192.

(5) (a) Kasai, M.; Oda, M.; Kitahara, Y. *Chem. Lett.* **1978**, 217–218. (b) Maier, G.; Reisenauer, H. P.; Sayrac, T. *Chem. Ber.* **1982**, *115*, 2192–2201.

(6) (a) Allen, A. D.; Ma, J.; McAllister, M. A.; Tidwell, T. T.; Zhao, D.-c. *Acc. Chem. Res.* **1995**, *28*, 265–271. (b) Zhao, D.-c.; Allen, A. D.; Tidwell, T. T. *J. Am. Chem. Soc.* **1993**, *115*, 10097–10103. (c) Allen, A. D.; Lai, W.-Y.; Ma, J.; Tidwell, T. T. *J. Am. Chem. Soc.* **1994**, *116*, 2625–2626. (d) Allen, A. D.; Ji, R.; Lai, W.-Y.; Ma, J.; Tidwell, T. T. *Heteroat. Chem.* **1994**, *5*, 235–244. (e) McAllister, M. A.; Tidwell, T. T. *J. Am. Chem. Soc.* **1994**, *116*, 7233–7238. (f) Werstiuk, N. H.; Ma, J.; McAllister M. A.; Tidwell, T. T.; Zhao, D.-c. *J. Chem. Soc., Faraday Trans.* **1994**, *90*, 3383–3390. (g) Gong, L.; McAllister, M. A.; Tidwell, T. T. *J. Am. Chem. Soc.* **1991**, *113*, 6021–6028. (h) McAllister, M. A.; Tidwell, T. T. *J. Org. Chem.* **1994**, *59*, 4506–4515.

(7) (a) Wagner, B. D.; Zgierski, M. Z.; Lusztyk, J. *J. Am. Chem. Soc.* **1994**, *116*, 6433–6434. (b) Arnold, B. R.; Brown, C. E.; Lusztyk, J. *J. Am. Chem. Soc.* **1993**, *115*, 1576–1577.

(8) (a) Liebeskind, L. S.; Fengl, R. W.; Wirtz, K. R.; Shawe, T. T. *J. Org. Chem.* **1988**, *53*, 2482–2488. (b) Danheiser, R. L.; Sard, H. *Tetrahedron Lett.* **1983**, *24*, 23–26. (c) Ooms, P. H. J.; Scheeren, J. W.; Nivard, R. J. F. *Synthesis* **1975**, 639–641. (d) Smutny, E. J.; Caserio, M. C.; Roberts, J. D. *J. Am. Chem. Soc.* **1960**, *82*, 1793–1801.

(9) (a) Hehre, W. J.; Radom, L.; Schleyer, P. v. R.; Pople, J. A. *Ab Initio Molecular Orbital Theory*; Wiley: New York, 1986. (b) Frisch, M. J.; Trucks, G. W.; Head-Gordon, M.; Gill, P. M. W.; Wong, M. W.; Foresman, J. B.; Johnson, B. G.; Schlegel, H. B.; Robb, M. A.; Replogle, E. S.; Gomperts, R.; Andres, J. L.; Raghavachari, K.; Binkley, J. S.; Gonzalez, C.; Martin, R. L.; Fox, D. J.; Defrees, D. J.; Baker, J.; Stewart, J. J. P.; Pople, J. A. *Gaussian 92*; Gaussian, Inc.: Pittsburgh, PA, 1992.

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Table 1. Infrared Spectra and Ring Closure Kinetics of 1,2-Bis(ketenes) in CH_3CN

no.	R[1]	R[2]	ν_1, ν_2 (cm^{-1}) calc[d]	ν_1, ν_2 (cm^{-1}) obs[e]	I_1/I_2[a] calc[d]	I_1/I_2[a] obs[e]	k_{obs} (s^{-1})[b]	ΣSE[c]
1a	H	Ph		2103, 2127		0.55	$(1.70 \pm 0.13) \times 10^{-4}$	4.8
1b	Ph	Ph		2096, 2110		0.75	$(3.89 \pm 0.15) \times 10^{-2}$	1.8
1c	Me	Me	2098, 2113	2092,2114	1.41	1.82		0.0
5[f]	Me_3Si	Me_3Si	2089, 2090[g]	2084[f]	1.60[g]			23.0
6	Me_3Si	Ph		2076[h]			2.03×10^{-6} [h]	12.4
7	Me_3Si	Me		2101[h]			4.37×10^{-6} [h]	11.5
8	Me	Ph		2093, 2112		0.60		0.9
9	EtO	Me_3Si		2090, 2104		1.33		−3.0
10	CN	Ph		2116, 2140		2.68		1.5
11	Br	Ph		2105, 2132		0.98		(−6.8)[i]
3			2062, 2133	2072, 2128	0.96	0.81	1.9×10^4	

[a] Relative IR intensities. [b] 25.0 °C unless noted. [c] Calculated ketene stabilization energy of substituents, ref 6h. [d] MP2/6-31G*//MP2/6-31G* for **1c** and **5**, HF/6-31G*//HF/6-31G* for **3**. [e] (23 ± 2)°C. [f] Reference 1b. [g] For SiH_3. [h] Reference 6c. [i] Using the SE value of −7.7 of Cl for Br.

Table 2. Kinetic Parameters for Conversion of 1,3-Butadiene-1,4-diones (O=C=CRCR[1]C=C=O) to Cyclobutenediones

R, R[1]	solvent	T[a]	k_{obs}[b]	E_a[c]	$\Delta H^‡$ [c]	$\Delta S^‡$ [d]
Ph, Ph (**1b**)	isooctane	5.5	$(5.51 \pm 0.13) \times 10^{-3}$			
	hexanes	25.0	$(3.89 \pm 0.15) \times 10^{-2}$	16.8	16.3	−10.4
	isooctane	33.5	$(9.03 \pm 0.25) \times 10^{-2}$			
	$CDCl_3$	5.5	$(2.29 \pm 0.10) \times 10^{-2}$			
	$CDCl_3$	25.0	$(1.26 \pm 0.01) \times 10^{-1}$	15.4	14.8	−12.8
	$CDCl_3$	33.5	$(3.01 \pm 0.18) \times 10^{-1}$			
Ph, H (**1a**)	isooctane	24.0	$(1.70 \pm 0.13) \times 10^{-4}$	19.7	19.1	−11.7
	isooctane	33.5	$(4.19 \pm 0.10) \times 10^{-4}$			
	isooctane	54.5	$(3.70 \pm 0.12) \times 10^{-3}$			
	$CDCl_3$	24.0	$(5.56 \pm 0.09) \times 10^{-4}$	19.6	19.0	−9.5
	$CDCl_3$	33.5	$(1.62 \pm 0.05) \times 10^{-3}$			
	$CDCl_3$	54.5	$(1.23 \pm 0.02) \times 10^{-2}$			

[a] In °C. [b] In s^{-1}. [c] In kcal/mol. [d] In cal/(K·mol).

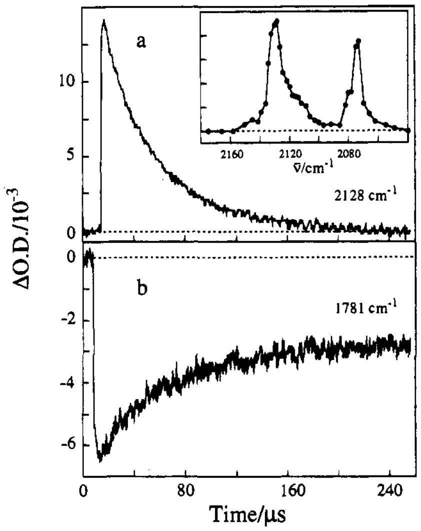

Figure 1. Transient IR absorption traces observed upon 308 nm photolysis of benzocyclobutenedione (**12**) in CH_3CN. (a) Generation and decay of bisketene **3** at 2128 cm^{-1}; single-exponential fit gave a lifetime of 52 μs. The inset shows the transient IR spectrum of the bisketene. (b) Bleach and partial recovery of the precursor carbonyl band at 1781 cm^{-1}; single-exponential fit of the growth gave a lifetime of 54 μs.

further tested these predictions for the monophenyl and diphenyl bisketenes **1a** and **1b**. Upon photolysis of 3-phenylcyclobut-3-ene-1,2-dione (**2a**) in $CDCl_3$ at 2 °C in an NMR tube with 350 nm light for 8 min, the ^1H NMR signals of **2a** decreased and spectra consistent with the formation of **1a** appeared: ^1H NMR ($CDCl_3$) δ 3.62 (s, 1), 7.14 (m, 2), 7.34 (m, 3); IR ($CDCl_3$) 2127 (vs), 2103 (vs). The **2a**/**1a** ratio was 55/45 and remained constant on further photolysis, suggesting that a photostationary state was attained. The formation of phenylacetylene from a bis(decarbonylation) reaction was observed, as has been found in other such photolyses.[6a-d] After cessation of photolysis, the conversion of **1a** back to **2a** was monitored by ^1H NMR by observing the decay of the signal at δ 3.62 or the increase of the signal at δ 9.57 for the cyclobutenyl hydrogen of **2a**, with approximate rate constants of 7×10^{-4} s^{-1} at 22 °C for both processes. The decrease in UV absorption due to **1a** or the increase of the absorption due to **2a** gave good first-order kinetics, with the same rate constant for either process (Table 2).

Photolysis of diphenylcyclobutenedione (**2b**) in pentane at −195 °C gave a change in the UV spectrum with a decrease in the λ_{max} of **2b** at 260 and 320 nm and formation of bisketene **1b** with strong absorption at low wavelength and a shoulder at 220 nm, which re-formed **2b** with good first-order kinetics (Table 2). The UV spectrum of diphenylacetylene was also observed. At 33.5 °C the rate of ring closure of the 2,3-diphenyl bisketene **1b** exceeded that of the monophenyl analogue **1a** by factors of 216 (isooctane) and 186 ($CDCl_3$). The greater reactivity of **1b** is consistent with the lower stabilizing influence of phenyl as a ketene substituent relative to hydrogen, as shown by the calculated (HF/6-31G*//HF/6-31G*) $\Delta E = -2.6$ kcal/mol for the isodesmic reaction of eq 2.[6h]

$$PhCH{=}C{=}O + CH_2{=}CH_2 \xrightarrow{\Delta E = -2.6\ \text{kcal/mol}} CH_2{=}C{=}O + PhCH{=}CH_2 \qquad (2)$$

Bisketenes **1c** and **8**−**11** were more reactive in ring closure than **1a** and **1b** and could not be observed at room temperature by conventional photolysis and detection techniques. Under TRIR conditions these species were observed, but the rate constants for their ring closure were too slow to measure with our apparatus. These results are consistent with simple predictions based upon the *ab initio* calculated stabilizing energies of ketenes for different substituent groups. Thus the stabilization energy ΣSE (Table 1) for **1a** exceeds that of the more reactive **1b**, while **1c** and **8**−**11**, which have lower ΣSE values, could not be observed. The silyl-stabilized ketenes **7**, **6**, and **5** have progressively larger ΣSE values than **1a** and are progressively less reactive.

In conclusion, laser flash photolysis combined with time-resolved infrared spectroscopy permits the direct observation of the *o*-quinoketene **3** and the first measurement of the kinetics of its ring closure. Conventional photolysis and UV detection have elucidated the formation of a wide variety of 1,2-bis(ketenes) and their ring closure back to the parent cyclobutenediones. A span of reactivities of 10^{10} between **3** and **6** has been measured, while the bis(trimethylsilyl) derivative **5** undergoes ring closure at an undetectably slow rate. Molecular orbital calculations illuminate the factors governing the relative stabilities of these interconverting isomers.

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