J. Am. Chem. Soc. **1994,** *116,* 7233–7238

Ab Initio Calculations of the Ring Opening of Cyclobutene-1,2-diones and Conformational Properties of the Product 1,3-Butadiene-1,4-diones (Bisketenes)

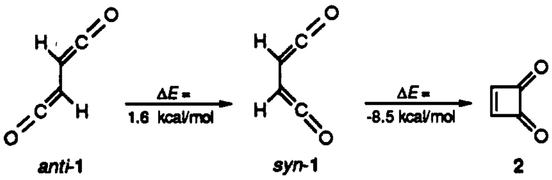
Michael A. McAllister and Thomas T. Tidwell*

Contribution from the Department of Chemistry, University of Toronto, Toronto, Ontario, Canada M5S 1A1

Received July 23, 1993. Revised Manuscript Received April 11, 1994®

Abstract: *Ab initio* molecular orbital calculations of the structures and energies in the ring opening of cyclobutene-1,2-diones to form 1,3-butadiene-1,4-diones (bisketenes) show that the reaction is endothermic by 3.2 kcal/mol for the hydrogen substituted case, but with a high barrier of 30.8 kcal/mol, at the MP2/6-31G* + ZPVE//MP2/6-31G* level. Substituents SiH_3 favor the ring opened bisketene form by 3.9 and 4.4 kcal/mol per group, and lower the barrier by 1.4 and 1.6 kcal/mol per group. Fluoro substituents disfavor the bisketene by 10.3 and 6.7 kcal/mol per group, but one fluorine increases the barrier for ring opening by only 0.8 kcal/mol, while the barrier is 0.9 kcal/mol less for the difluoro derivative than for the parent, indicating that any influence of product destabilization by fluorine on the barrier is compensated by ground state destabilization by fluorine tending to decrease the barrier for ring opening. In all cases twisted conformations are the lowest energy minima for the bisketenes and are favored over the planar forms, which are transition structures for rotation around the single C–C bond. The calculated energies, including enthalpy and entropy changes, are in good agreement with available experimental data. For cyclobutene, cyclobutenone, and cyclobutenedione there is no correspondence between the magnitude of the barriers of the reaction and the overall energy changes, and for cyclobutenone this is attributed partly to a favorable dipolar transition state interaction.

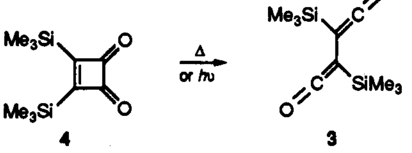
Recently it was predicted on the basis of molecular orbital calculations at the HF/6-31G*//HF/6-31G* *ab initio* level for planar 1,3-butadiene-1,4-dione (**1**) and cyclobutene-1,2-dione (**2**) that the latter is the more stable by only 6.9 kcal/mol (equation 1).[1a] The calculated energy change of 7.6 kcal/mol for eq 2 demonstrates a large ketene stabilizing effect for electropositive groups such as SiH_3 and permits the further prediction that with an appropriate choice of substituents bisketenes would be more stable than the isomeric cyclobutenediones.[1a] This has now been verified experimentally by the formation of the persistent and long-lived 2,3-bis(trimethylsilyl)-1,3-butadiene-1,4-dione (**3**) from the cyclobutenedione **4** (eq 3).[1b,c] A rich chemistry of **3** and related compounds has already been revealed,[1b–f] and the current study deals with calculations of the barrier to ring opening of **2** and substituted derivatives, the energies and conformational properties of the product bisketenes, and comparison to the ring openings of cyclobutene and cyclobutenone.



(1)

anti-**1** *syn*-**1** **2**

$$SiH_3CH{=}C{=}O + CH_2{=}CH_2 \xrightarrow[7.6\ kcal/mol]{\Delta E =} SiH_3CH{=}CH_2 + CH_2{=}C{=}O \qquad (2)$$



(3)

4 **3**

The question of the conformational properties of conjugated unsaturated systems is of great current interest. The structures of 1,3-butadiene,[2a,b] acrolein,[2a] various thia-1,3-butadienes,[2c] oxa- and aza-1,3-butadienes,[2d] other heterobutadienes,[2d,e] and methyl-1,3-butadienes[2f] have recently been examined at high levels of theory, and at the MP2/6-31G*//MP2/6-31G* level 1,3-butadiene has relative energies at fixed torsional angles of 0° (*syn*), 90°, and 180° (*anti*) of 3.59, 5.68, and 0.00 kcal/mol, respectively, while for acrolein at the same level of theory the relative energies are 1.47, 8.16, and 0.00 kcal/mol respectively.[2a] The experimental[3a,b] rotational barrier of 1,3-butadiene of between 3.9 and 4.9 kcal/mol is close to the calculated barrier,[2a] and the cyclobutene/1,3-butadiene interconversion has been examined at various levels of theory.[2g]

There has also been a great deal of experimental study of the thermal ring opening of cyclobutene[4a] and substituted cyclobutenes[4b–g] to butadienes, and the photochemical ring opening has also been of interest.[4h] The ring opening of cyclobutenones

---

® Abstract published in *Advance ACS Abstracts*. July 1, 1994.

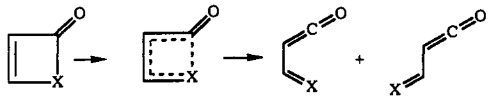
(1) (a) Gong, L.; McAllister, M. A.; Tidwell, T. T. *J. Am. Chem. Soc.* **1991,** *113,* 6021–6028. (b) Zhao, D.; Tidwell, T. T. *J. Am. Chem. Soc.* **1992,** *114,* 10980–10981. (c) Zhao, D.; Allen, A. D.; Tidwell, T. T. *J. Am. Chem. Soc.* **1993,** *115,* 10097–10103. (d) Allen, A. D.; Lai, W.-Y.; Ma, J.; Tidwell, T. T. *J. Am. Chem. Soc.* **1994,** *116,* 2625–2626. (e) Allen, A. D.; Ma, J.; McAllister, M. A.; Tidwell, T. T. Submitted for publication. (f) Werstiuk, N.; Ma, J.; McAllister, M. A.; Tidwell, T. T.; Zhao, D. Submitted for publication. (g) McAllister, M. A.; Tidwell, T. T. *J. Org. Chem.* **1994,** *59,* in press.

(2) (a) Wiberg, K. B.; Rosenberg, R. E.; Rablen, P. R. *J. Am. Chem. Soc.* **1991,** *113,* 2890–2898. (b) Wiberg, K. B.; Rosenberg, R. E. *J. Am. Chem. Soc.* **1990,** *112,* 1509–1519. (c) Yu, H.; Chan, W.-T.; Goddard, J. D. *J. Am. Chem. Soc.* **1990,** *112,* 7529–7537. (d) Wiberg, K. B.; Rablen, P. R.; Marquez, M. *J. Am. Chem. Soc.* **1992,** *114,* 8654–8668. (e) Nguyen, M. T.; Ha, T.; More O'Ferrall, R. A. *J. Org. Chem.* **1990,** *55,* 3251–3256. (f) Guo, H.; Karplus, M. *J. Mol. Struct. (Theochem)* **1993,** *260,* 347–393. (g) Spellmeyer, D. C.; Houk, K. N. *J. Am. Chem. Soc.* **1988,** *110,* 3412–3416.

(3) (a) Lipnick, R. L.; Garbisch, E. W., Jr. *J. Am. Chem. Soc.* **1973,** *95,* 6370–6375. (b) Carreira, L. A. *J. Chem. Phys.* **1975,** *62,* 3851–3854.

(4) (a) Cooper, W.; Walters, W. D. *J. Am. Chem. Soc.* **1958,** *80,* 4220–4224. (b) Pomerantz, M.; Hartman, P. H. *Tetrahedron Lett.* **1968,** 991–993. (c) Frey, H.M.; Pope, B. M.; Skinner, R. F. *Trans. Faraday Soc.* **1967,** *63,* 1166–1170. (d) Brauman, J. I.; Archie, W. C., Jr. *Tetrahedron* **1971,** *27,* 1275–1280. (e) Dolbier, W.R., Jr.; Koroniak, H.; Burton, D. J.; Heinze, P. L.; Bailey, A. R.; Shaw, G. S.; Hansen, S. W. *J. Am. Chem. Soc.* **1987,** *109,* 219–225. (f) Kirmse, W.; Rondan, N.G.; Houk, K. N. *J. Am. Chem. Soc.* **1984,** *106,* 7989–7991. (g) Schlag, E. W.; Peatman, W. B. *J. Am. Chem. Soc.* **1964,** *86,* 1676–1679. (h) Leigh, W. J. *Can. J. Chem.* **1993,** *71,* 147–155.

0002-7863/94/1516-7233$04.50/0



X = CH_2	−1.0 (5)	27.2 (8)	0.0	−1.6 (11)
O	18.0 (6)	19.3 (9)	0.0	0.5 (12)
NH	10.0 (7)	22.5 (10)	0.0	0.1 (13)

Figure 1. Calculated (MP2/6-31G**//HF/6-31G**) relative energies (kcal/mol) for ketene-forming reactions.[2e]

to vinylketenes has been the subject of mechanistic study[5a,b] and is of great utility in synthesis.[5c–e] The thermal ring openings of substituted cyclobutenes[6a–e] and methylenecyclobutenes[6f–h] have been the subject of continuing theoretical study.

Calculations of the structures of the reactants **5–7** and transition states **8–10** leading to vinylketene (**11**), formylketene (**12**), and imidoylketene (**13**), respectively, have been reported[2e] at the HF/6-31G** level, and the relative energies for single point energy calculations at the MP2/6-31G** level found for these structures are shown (Figure 1). Other single point energy calculations for this geometry gave slightly different values.[2e]

The calculations revealed that the ring opened ketenyl forms were significantly more stable for the formyl- and imidoylketenes, and these were slightly more stable in *syn*-planar geometries. Vinylketene (**11**) and cyclobutenone (**5**) were calculated to be of almost equal stability, but interestingly the largest barriers in either direction are found for this case.[2e]

Because of the general interest in cyclobutene/butadiene structures and interconversions, and the fascinating chemistry which has been found for **3** and **4**,[1b–f] we have carried out *ab initio* calculations on the structures and conformations of **1** and **2** and their connecting transition structure. To elucidate the effect of substituents on the reaction, the structures and energies of **1** and **2** substituted with various combinations of the ketene stabilizing group SiH_3 and the highly destabilizing fluoro group have also been examined . For comparative purposes the cyclobutene/butadiene and cyclobutenone/vinylketene pairs have been examined at the same levels of theory. These studies are also revealing as to the electronic structure of cyclobutene-1,2-diones such as **2** and **4**, and substituent effects on these compounds, which are also of theoretical importance because of their aromatic properties,[7a,b] and are important synthetic intermediates.[5c–e,8]

Results

The *ab initio* molecular orbital calculations were carried out using the Gaussian 90 and Gaussian 92 series of programs[9a] on Hewlett Packard 9000-750 and IBM RS/6000-530 minicomputers. All geometries were gradient optimized using the standard split valence HF/6-31G* basis set,[9b,c] with the Berny Optimizer with no geometrical constraints.[9b] The orders (number of negative diagonal elements of the Hessian matrix of all critical points) were determined at the HF/6-31G* level by analytical differentiation of the restricted Hartree–Fock wave function. Geometries which were optimized at the MP2/6-31G* level were also order checked at that level. The frozen core approximation was not used.

Energies calculated for optimized geometries at the HF/6-31G*//HF/6-31G* and MP2/6-31G*//MP2/6-31G* levels for cyclobutene-1,2-dione (**2**) and 3,4-difluorocyclobutene-1,2-dione (**16**), their respective transition structures for ring opening **14** and **22**, and the twist, transoid, and ciscoid conformations of the ring-opened unsubstituted bisketene (**1a–c**) are given in Table 1, as well as the HF/6-31G*//HF/6-31G* energies for cyclobutenediones **15–19**, transition structures **20–24**, and bisketenes **25–29** with the substituent pairs R_1, R_2 = F, H; SiH_3, H; F, F; SiH_3, SiH_3; and SiH_3, F, respectively. Because of limitations on the available computer time all the geometries could not be optimized at the MP2/6-31G* level, but single point MP2/6-31G*//HF/6-31G* energies were calculated for all the cyclobutenediones **2**, **15–19**, their transition structures for ring opening (**14**, **20–24**), and for the energy minima twisted bisketenes **1a** and **25a–29a**. Calculated zero point vibrational energies (ZPVE), obtained from calculated vibrational frequencies scaled by 0.9, are included in Table 1.[9b,d] In Table 2 are given the energies at both levels of theory for cyclobutene (**30**) and cyclobutenone (**5**), their transition structures for ring opening, and products. Single point MP2/6-31G*//HF/6-31G* energies for **5** and **30** and their transition states for ring opening are also reported. The relative energies from Tables 1 and 2 are summarized in Table 3, along with calculated enthalpies and entropies of reaction and activation parameters at 298 K derived by the method of Jorgensen *et al.*[9e] from the calculated zero point vibrational energies. The bond distances and bond angles of the structures are summarized in Table 4, and are given in full in Tables 5 and 6 (Supplementary Material). The reactant, transition state, and most stable product for the ring opening of the parent cyclobutenedione **2** and the $(SiH_3)_2$-substituted derivative **18** are depicted in Figures 2 and 3, respectively.

Energies

There are significant decreases in all of the relative energies in Table 3 in going from the HF/6-31G* to the MP2/6-31G* level, and it is clear that at least the MP2/6-31G* level is needed to obtain reliable values. Significantly, for the five cases in which E_a or ΔE were obtained at the MP2/6-31G* + ZPVE level using both the MP2/6-31G* and the HF/6-31G* optimized geometries, the results were almost identical, with an average difference of 0.2 kcal/mol, and the largest difference being 0.6 kcal/mol for the transition state **14** for the ring opening of unsubstituted cyclobutenedione **2** (Table 3). This result lends confidence that the energies for the other structures calculated at the MP2/6-31G* + ZPVE//HF/6-31G* level can be meaningfully compared to the energies calculated for structures optimized at MP2/6-31G*. Also, as has been noted,[2e,8] energies for cyclobutene ring opening calculated at the MP2/6-31G* level have been found to be closer to the true values than those at higher levels.

The calculated barriers for ring opening of cyclobutene (**30**), cyclobutenone (**5**), and cyclobutenedione (**2**) (Table 3) decrease

---

(5) (a) Huisgen, R.; Mayr, H. *J. Chem. Soc., Chem. Commun.* **1976**, 55–56. (b) Mayr, H.; Huisgen, R. *J. Chem. Soc., Chem. Commun.* **1976**, 57–58. (c) Moore, H.W.; Yerxa, R. B. *Chemtracts: Org. Chem.* **1992**, *5*, 273–313. (d) Liebeskind, L. S.; Granberg, K. L.; Zhang, J. *J. Org. Chem.* **1992**, *57*, 4345–4352. (e) Danheiser, R. L.; Brisbois, R. G.; Kowalczyk J. J.; Miller, R. T. *J. Am. Chem. Soc.* **1990**, *112*, 3093–3100.

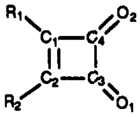
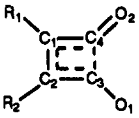
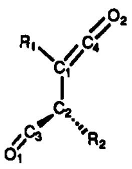
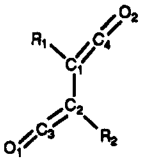
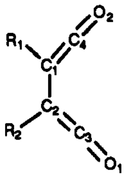
(6) (a) Breulet, J.; Schaefer, H. F., III. *J. Am. Chem. Soc.* **1984**, *106*, 1221–1226. (b) Rondan, N. G.; Houk, K. N. *J. Am. Chem. Soc.* **1985**, *107*, 2099–2111. (c) Rudolf, K.; Spellmeyer, D. C.; Houk, K. N. *J. Org. Chem.* **1987**, *52*, 3708–3710. (d) Bachrach, S. M.; Liu, M. *J. Org. Chem.* **1992**, *57*, 2040–2047. (e) Niwayama, S.; Houk, K. N. *Tetrahedron Lett.* **1993**, *34*, 1251–1254. (f) Pasto, D. J.; Yang, S.-H. *J. Org. Chem.* **1989**, *54*, 3544–3549. (g) Pasto, D. J.; Kong, W. *J. Org. Chem.* **1989**, *54*, 4028–4033. (h) Rey, J. C.; Rodriquez, J.; de Lera, A. R. *Tetrahedron Lett.* **1993**, *34*, 6293–6296.

(7) (a) West, R. Ed.; *Oxocarbons*; Academic Press: New York, 1980. (b) Cava, M. P.; Mitchell, M. J. *Cyclobutadiene and Related Compounds*; Academic Press: New York, 1967. (c) Allen, A. D.; Tidwell, T. T. *Adv. Carbocation Chem.* **1989**, *1*, 1–44. (d) McAllister, M. A.; Tidwell, T. T. *Croat. Chim. Acta* **1992**, *65*, 633–653.

(8) (a) Sidduri, A. R.; Budries, N.; Laine, R. M.; Knochel, P. *Tetrahedron Lett.* **1992**, *33*, 7515–7518. (b) Ohno, M.; Yamamoto, Y.; Shirasaki, Y.; Eguchi, S. *J. Chem. Soc., Perkin Trans. 1* **1993**, 263–271. (c) Kinney, W. A. *Tetrahedron Lett.* **1993**, *34*, 2715–2718. (d) Schmidt, A. H. *Synthesis* **1980**, 961–994. (e) Schmidt, A.H.; Ried, W. *Synthesis* **1978**, 869–880. (f) Liebeskind, L. S.; Yu, M. S.; Fengl, R.W. *J. Org. Chem.* **1993**, *58*, 3543–3549.

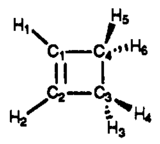
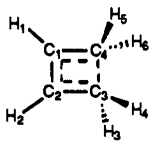
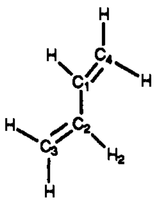
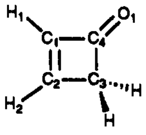
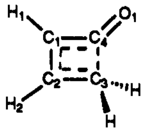
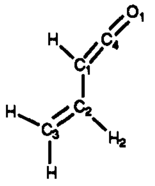
(9) (a) Frisch, M. J.; Trucks, G. W.; Head-Gordon, M.; Gill, P. M. W.; Wong, M. W.; Foresman, J. B.; Johnson, B. G.; Schlegel, H. B.; Robb, M. A.; Replogle, E. S.; Gomperts, R.; Andres, J. L.; Raghavachari, K.; Binkley, J. S.; Gonzalez, C.; Martin, R. L.; Fox, D. J.; Defrees, D. J.; Baker, J.; Stewart, J. J. P.; Pople, J. A. *Gaussian 92*, Gaussian, Inc.: Pittsburgh, PA, 1992. (b) Hehre, W. J.; Radom, L.; Schleyer, P. v. R.; Pople, J. A. *Ab Initio Molecular Orbital Theory*; Wiley-Interscience: New York, 1986. (c) Hariharan, P. C.; Pople, J. A. *Theor. Chim. Acta* **1973**, *28*, 213–221. (d) Houk, K. N.; Gustafson, S. M.; Black, K. A. *J. Am. Chem. Soc.* **1992**, *114*, 8565–8572. (e) Jorgensen, W. L.; Lim, D.; Blake, J. F. *J. Am. Chem. Soc.* **1993**, *115*, 2936–2942.

Table 1. Calculated Energies and Dipole Moments of Cyclobutenediones, Transition States, and Bisketenes[a-g]

	 **2,15-19**	 **14, 20-24**	 **1, 25a-29a**	 **1,25b-29b**	 **1, 25c-29c**
R_1, R_2 = H	**2**	**14**	**1a**	**1b**	**1c**
E^{HF}[a]	302.2968(0)	302.2195(1)	302.2908(0)	302.2858(1)	302.2832(1)
$E_{\mathrm{rel}}^{\mathrm{HF}}$[b]	0.0	48.5	3.8	6.9	8.5
HF ZPVE[c]	30.6	28.4	29.2	28.8	28.8
$E_{\mathrm{rel}}^{\mathrm{HF+ZPVE}}$[b]	0.0	46.3	2.4	5.1	6.7
$E^{\mathrm{MP2//HF}}$[d]	303.1351	303.0834	303.1274		
$E_{\mathrm{rel}}^{\mathrm{MP2//HF}}$[b]	0.0	32.4	4.8		
$E_{\mathrm{rel}}^{\mathrm{MP2+Z//HF}}$[b]	0.0	30.2	3.4		
E^{MP2}[e]	303.1658(0)	303.1142(1)	303.1595(0)	303.1546(1)	303.1528(1)
$E_{\mathrm{rel}}^{\mathrm{MP2}}$[b]	0.0	32.4	4.0	6.9	8.5
MP2 ZPVE[c]	27.9	26.3	27.1	26.6	26.6
$E_{\mathrm{rel}}^{\mathrm{MP2+ZPVE}}$[b]	0.0	30.8	3.2	5.6	7.2
μ (D)[f]	4.83	4.33	1.91	0.0	2.84
R_1 = F, R_2 = H	**15**	**20**	**25a**	**25b**	**25c**
E^{HF}[a]	401.1408(0)	401.0617(1)	401.1147(0)	401.1100(1)	401.1055(1)
$E_{\mathrm{rel}}^{\mathrm{HF}}$[b]	0.0	49.7	14.7	19.4	22.2
HF ZPVE[c]	26.1	23.9	24.7	24.4	24.3
$E_{\mathrm{rel}}^{\mathrm{HF+ZPVE}}$[b]	0.0	47.5	13.3	17.7	20.4
$E^{\mathrm{MP2//HF}}$[d]	402.1477	402.0948	402.1237		
$E_{\mathrm{rel}}^{\mathrm{MP2//HF}}$[b]	0.0	33.2	15.1		
$E_{\mathrm{rel}}^{\mathrm{MP2+Z//HF}}$[b]	0.0	31.0	13.7		
μ (D)[f]	3.87	3.23	1.67	1.64	1.61
R_1 = SiH$_3$, R_2 = H	**16**	**21**	**26a**		
E^{HF}[a]	592.3809(0)	592.3047(1)	592.3803(0)		
$E_{\mathrm{rel}}^{\mathrm{HF}}$[b]	0.0	47.8	0.3		
HF ZPVE[c]	39.9	37.6	38.8		
$E_{\mathrm{rel}}^{\mathrm{HF+ZPVE}}$[b]	0.8	46.6	0.0		
$E^{\mathrm{MP2//HF}}$[d]	593.2983	593.2487	593.2974		
$E_{\mathrm{rel}}^{\mathrm{MP2//HF}}$[b]	0.0	31.1	0.6		
$E_{\mathrm{rel}}^{\mathrm{MP2+Z//HF}}$[b]	0.5	29.3	0.0		
μ (D)[f]	4.81	4.33	1.59		
R_1, R_2 = F	**17**	**22**	**27a**		
E^{HF}[a]	499.9780(0)	499.8975(1)	499.9413(0)	499.9305(1)	499.9209(1)
$E_{\mathrm{rel}}^{\mathrm{HF}}$[b]	0.0	50.5	23.0	26.7	35.8
HF ZPVE[c]	21.6	19.5	20.1	19.9	19.8
$E_{\mathrm{rel}}^{\mathrm{HF+ZPVE}}$[b]	0.0	48.4	21.5	25.0	34.0
$E^{\mathrm{MP2//HF}}$[d]	501.1530	501.1020	501.1181		
$E_{\mathrm{rel}}^{\mathrm{MP2//HF}}$[b]	0.0	32.0	21.9		
$E_{\mathrm{rel}}^{\mathrm{MP2+Z//HF}}$[b]	0.0	29.9	20.4		
E^{MP2}[e]	501.1919	501.1408			
$E_{\mathrm{rel}}^{\mathrm{MP2}}$	0.0	32.1			
$E_{\mathrm{rel}}^{\mathrm{MP2+Z}}$[b,h]	0.0	29.9			
μ (D)[f]	2.84	1.59	0.68	0.0	0.26
R_1, R_2 = SiH$_3$	**18**	**23**	**28a**		
E^{HF}[a]	882.4633(0)	882.3890(1)	882.4696(0)		
$E_{\mathrm{rel}}^{\mathrm{HF}}$[b]	3.9	50.5	0.0		
HF ZPVE[c]	49.1	46.9	48.4		
$E_{\mathrm{rel}}^{\mathrm{HF+ZPVE}}$[b]	4.6	49.0	0.0		
$E^{\mathrm{MP2//HF}}$[d]	883.4612	883.4144	883.4679		
$E_{\mathrm{rel}}^{\mathrm{MP2//HF}}$[b]	4.2	33.6	0.0		
$E_{\mathrm{rel}}^{\mathrm{MP2+Z//HF}}$[b]	4.9	32.1	0.0		
μ (D)[f]	4.78	4.41	1.22		
R_1 = SiH$_3$; R_2 = F	**19**	**24**	**29a**		
E^{HF}[a]	691.2275(0)	691.1484(1)	691.2063(0)		
$E_{\mathrm{rel}}^{\mathrm{HF}}$[b]	0.0	49.6	13.3		
HF ZPVE[c]	35.5	33.1	34.2		
$E_{\mathrm{rel}}^{\mathrm{HF+ZPVE}}$[b]	0.0	47.2	12.0		
$E^{\mathrm{MP2//HF}}$[d]	692.3138	692.2606	692.2928		
$E_{\mathrm{rel}}^{\mathrm{MP2//HF}}$[b]	0.0	33.4	13.2		
$E_{\mathrm{rel}}^{\mathrm{MP2+Z//HF}}$[b]	0.0	31.0	11.9		
μ (D)[f]	3.99	3.42	1.45		

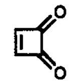
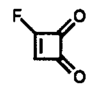
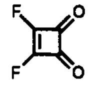
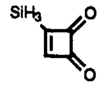
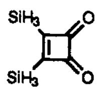
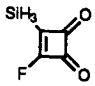
[a] E^{HF}: HF/6-31G*//HF6-31G* energy (–hartrees). [b] Relative energy (kcal/mol). [c] ZPVE: zero point vibrational energy (kcal/mol) scaled by 0.9. [d] $E^{\mathrm{MP2//HF}}$: MP2/6-31G*//HF/6-31G* energy (–hartrees). [e] E^{MP2}: MP2/6-31G*//MP2/6-31G* energy (–hartrees). [f] μ: dipole moment (D) HF/6-31G*. [g] Number of critical points in parentheses. [h] Compared using HF ZPVE.

Table 2. Calculated Energies and Dipole Moments of Cyclobutenones and Cyclobutenes, Transition States, Vinylketene, and Dienes[a–g]

	 30	 31	 32	 5	 8	 11
$E^{\mathrm{HF}\,a}$	154.8996(0)	154.8248(1)	154.9197(0)	228.6039(0)	228.5407(1)	228.6070(0)
$E_{\mathrm{rel}}^{\mathrm{HF}\,b}$	0.0	46.9	-12.6	0.0	39.7	-1.9
HF ZPVE[c]	52.7	51.0	51.7	41.7	39.8	40.3
$E_{\mathrm{rel}}^{\mathrm{HF+ZPVE}\,b}$	0.0	45.2	-13.3	0.0	37.8	-3.3
$E^{\mathrm{MP2//HF}\,d}$	155.4091	155.3495		229.2761	229.2306	
$E_{\mathrm{rel}}^{\mathrm{MP2//HF}\,b}$	0.0	37.4		0.0	28.6	
$E_{\mathrm{rel}}^{\mathrm{MP2+Z//HF}\,b}$	0.0	35.7		0.0	26.7	
$E^{\mathrm{MP2}\,e}$	155.4102(0)	155.3506(1)	155.4417(0)	229.3012(0)	229.2561(1)	229.3028(0)
$E_{\mathrm{rel}}^{\mathrm{MP2}\,b}$	0.0	37.4	-19.8	0.0	28.2	-1.0
MP2 ZPVE[c]	49.9	48.3	48.8	39.0	37.5	37.9
$E_{\mathrm{rel}}^{\mathrm{MP2}}$ + ZPVE[b]	0.0	35.8	-20.9	0.0	26.7	-2.1
μ (D)[f]	0.03	0.23	0.00	3.74	2.91	1.21

[a] E^{HF}: HF/6-31G*//HF/6-31G* energy (–hartrees). [b] Relative energy (kcal/mol). [c] ZPVE: zero point vibrational energy (kcal/mol) scaled by 0.9. [d] $E^{\mathrm{MP2//HF}}$: MP2/6-31G*//HF/6-31G* energy (–hartrees). [e] E^{MP2}: MP2/6-31G*//MP2/6-31G* energy (–hartrees). [f] μ: dipole moment (D) HF/6-31G*. [g] Number of critical points in parentheses.

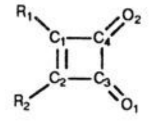
Table 3. Summary of Relative Energies (kcal/mol) and Entropy Changes (cal mol^{-1} K^{-1}) in Ring Opening of Cyclobutenes, Cyclobutenones, and Cyclobutenediones

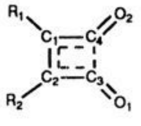
	level	E_a	$\Delta G^{\ddagger}$	$\Delta H^{\ddagger}$	$\Delta S^{\ddagger}$	ΔE	ΔG	ΔH	ΔS
 30	HF//HF[a]	45.2	44.5	44.5	0.0	-13.3	-15.3	-13.8	5.0
	MP2//HF[b]	35.7	35.0	35.0	0.0				
	MP2//MP2[c]	35.8	35.1	35.0	-0.2	-20.9	-23.0	-21.5	5.0
 5	HF//HF[a]	37.8	37.2	37.3	0.3	-3.3	-5.4	-4.1	4.3
	MP2//HF[b]	26.7	26.1	26.2	0.3				
	MP2//MP2[c]	26.7	25.7	25.8	0.2	-2.1	-4.0	-2.7	4.4
 2	HF//HF[a]	46.3	45.8	46.1	1.0	2.4	-0.6	1.4	6.7
	MP2//HF[b]	30.2	29.7	30.0	1.0	3.4	0.4	2.4	6.7
	MP2//MP2[c]	30.8	29.2	29.4	0.8	3.2	0.9	3.2	7.5
 15	HF/HF[a]	47.5	46.8	47.2	1.2	13.3	10.8	12.4	5.5
	MP2//HF[b]	31.0	30.3	30.7	1.2	13.7	11.2	12.8	5.5
 16	HF//HF[a]	48.4	47.7	48.0	1.0	21.5	18.5	20.6	7.0
	MP2//HF[b]	29.9	29.2	29.5	1.0	20.4	17.4	19.5	7.0
	MP2//MP2[c]	29.9							
 17	HF//HF[a]	45.8	45.0	45.5	1.7	-0.8	-2.8	-1.5	4.5
	MP2//HF[b]	28.8	28.0	28.5	1.7	-0.5	-2.5	-1.2	4.5
 18	HF//HF[a]	44.4	43.5	44.1	2.0	-4.6	-5.8	-5.0	2.9
	MP2//HF[b]	27.2	26.3	26.9	2.0	-4.9	-6.1	-5.3	2.9
 19	HF//HF[a]	47.2	48.2	47.4	-2.8	12.0	9.8	11.3	5.1
	MP2//HF[b]	31.0	32.0	31.2	-2.8	11.9	9.7	11.2	5.1

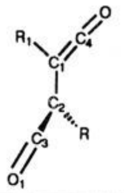
[a] HF/6-31G* + ZPVE//HF/6-31G*. [b] MP2/6-31G* + ZPVE//HF/6-31G*. [c] MP2/6-31G* + ZPVE//MP2/6-31G*.

as the level of calculation is increased from HF/6-31G* to MP2/6-31G*, by 9.4, 11.1, and 15.5 kcal/mol, respectively, and while cyclobutenone has the lowest calculated barrier at all levels the barrier for cyclobutenedione is almost the same as for cyclobutene at the HF/6-31G* level, but is 5.0 kcal/mol lower at the MP2 level. There is also no direct correspondence of the barriers to the overall energy change in the reaction, as the cyclobutene-to-butadiene interconversion is much the most favorable reaction,

Table 4. Selected Bond Lengths (changes in parentheses) (Å) and Dihedral Angles (deg) in Cyclobutenedione Ring Openings (HF/6-31G*)







R_1, R_2	compd no.	C_1C_4	C_3C_4	C_1C_2	C_2C_3	compd no.	C_1C_4	C_3C_4	C_1C_2	C_2C_3	$C_4C_1C_2C_3$	compd no.	C_1C_4	C_1C_2	C_2C_3	$C_4C_1C_2C_3$
H, H	**2**	1.502	1.558	1.337	1.502	**14**	1.381 (–0.121)	2.061 (0.503)	1.411 (0.074)	1.381 (–0.121)	24.4	**1a**	1.313	1.485	1.313	84.9
F, H	**15**	1.499	1.522	1.334	1.492	**20**	1.392 (–0.107)	2.098 (0.576)	1.407 (0.073)	1.369 (–0.123)	21.9	**25a**	1.312	1.460	1.320	84.8
F, F	**17**	1.488	1.547	1.334	1.488	**22**	1.373 (–0.115)	2.100 (0.553)	1.401 (0.067)	1.373 (–0.115)	20.2	**27a**	1.320	1.437	1.320	85.3
SiH_3, H	**16**	1.511	1.557	1.344	1.500	**21**	1.384 (–0.127)	2.044 (0.487)	1.421 (0.077)	1.384 (–0.116)	25.9	**26a**	1.315	1.498	1.313	86.4
SiH_3, SiH_3	**18**	1.511	1.554	1.352	1.511	**23**	1.387 (–0.124)	2.015 (0.461)	1.431 (0.079)	1.387 (–0.124)	27.8	**28a**	1.315	1.514	1.315	92.0
SiH_3, F	**19**	1.500	1.551	1.339	1.500	**24**	1.372 (–0.128)	2.093 (0.542)	1.414 (0.075)	1.396 (–0.104)	23.5	**29a**	1.311	1.473	1.322	85.4

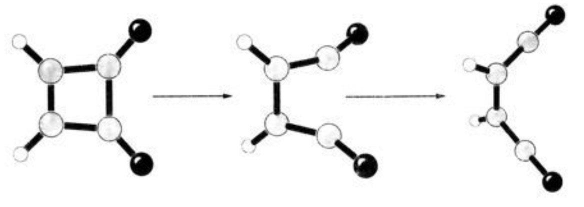


Figure 2. Reactant, transition structure, and product for ring opening of cyclobutenedione (**2**).

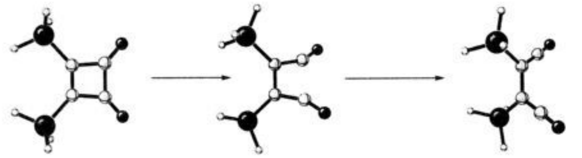


Figure 3. Reactant, transition structure, and product for ring opening of $(SiH_3)_2$-substituted cyclobutenedione **18**.

but also has the highest calculated barrier at the MP2 level. This phenomenon was noted before,[2e] and it may be attributed to the stabilizing zwitterionic character in the transition state for ring opening of cyclobutenone (**5**), with n–π donation by the carbonyl oxygen. This dipolar character has been cited[1a] as a prominent stabilizing effect in vinylketene (**11**), but it is less important in the symmetrical structures of cyclobutene and cyclobutenedione.

For cyclobutenone the barrier calculated here for MP2/6-31G* optimized geometries with ZPVE correction (26.7 kcal/mol) is 0.5 kcal/mol less than the lowest value obtained at various single point energy levels with the HF/6-31G** optimized geometry.[2e] This calculated barrier for ring opening of cyclobutenone of 26.7 kcal/mol is significantly less than the calculated (Table 3) or experimental[4a] barriers of 35.8 and 32.9 kcal/mol, respectively, for cyclobutene, and the experimental E_{act} for ring opening of the bis(trimethylsilyl)cyclobutenedione (**4**) of 29.4 kcal/mol[1c] is very close to the MP2 + ZPVE calculated barrier of 30.8 kcal/mol (Table 3) for the unsubstituted cyclobutenedione **2**, and the 27.2 kcal/mol barrier calculated for the $(SiH_3)_2$-substitued cyclobutenedione **18**. Only limited kinetic data on cyclobutenone ring opening are available,[5b] and there are no comparative data for the parent **5**.

The effect of substituents on the ring opening of cyclobutenediones at the MP2/6-31G* + ZPVE//HF/6-31G* level (Table 3) shows that fluorine compared to hydrogen strongly disfavors the ring opened bisketenes, by 10.3 and 6.7 kcal/mol for the first and second fluorines, respectively, as compared to the destabilizing effect of a single fluorine relative to hydrogen of 20.5 and 20.8 kcal/mol for monoketenes at the HF/6-31G*//HF/6-31G* [1a] and MP2/6-31G*//MP2/6-31G* [1g] levels, respectively. The smaller destabilizing effect of fluorine on the ring opening to the bisketene compared to the effect on a monoketene may be attributed to destabilization of the cyclobutene-1,2-dione by fluorine. As seen in resonance structure **33b** cyclobutenediones enjoy significant stabilization due to their 2πe⁻ aromatic character,[7a,b] but the electronegative fluorine would have a strong destabilizing effect on the adjacent positively charged ring.[7c,d] π donation by fluorine[7c,d] would not be stabilizing because of interference with the aromatic properties of the ring.

33a **33b**

Despite the major net effect of fluorine disfavoring the products of ring opening, the effect of fluorine relative to hydrogen on the transition states is a slight increase of 0.8 kcal/mol for one fluorine and a decrease of 1.1 kcal/mol for the second, so that the barrier for ring opening of difluorocyclobutenedione is calculated to be less than that of the parent, even though the former reaction is 17.0 kcal/mol less favorable. The small size of the substituent effect on the barrier is attributable both to the small change in the structure at the substituted carbons in the transition state, as discussed below, and also to the ground state destabilization by the fluorines which compensates for the effect on the barrier to ring opening of the influence of the highly destabilized fluorinated product.

The calculated stabilizing effect of SiH_3 on monoketenes relative to hydrogen at both the HF/6-31G*//HF/6-31G* [1a] and MP2/6-31G*//MP2/6-31G* [1g] level is 7.6 kcal/mol, while the successive replacement of hydrogens by SiH_3 on cyclobutenedione favors formation of the bisketene product by 3.9 and 4.4 kcal/mol, respectively (Table 3). Thus just as for fluorine the effect of the substituents is almost additive, but is only half the effect calculated for the monoketenes. This reduced influence of SiH_3 in favoring the bisketene form may also be partly due to a stabilizing substituent effect of silicon on the cyclobutenedione **33**. However, the available data on R_3Si groups adjacent to positive charge but with the C–Si bond orthogonal to the π system so that hyperconjugative stabilization is not possible, as is the case for **33**, are inconclusive as to the possible stabilization.[10]

The effect of SiH_3 relative to hydrogen on the transition states for the diketone ring opening is a decrease of 1.4 kcal/mol in the calculated barrier for one group, and 1.6 kcal/mol for the second. Thus the net effect of both substituents on the transition state is a decrease in the barrier of 3.0 kcal/mol, or about a third of the 8.3 kcal/mol calculated increase in the product stability. This significant effect shows that the stabilizing effect of silyl substituents on ketenes, which involves the interaction with the carbonyl carbon of the ketene, is already developing in the transition state. The combination of one SiH_3 and one F gives a barrier of 31.0 kcal/mol at the MP2/6-31G* + ZPVE//HF/6-31G* level (Table 3), as compared to those of 28.8 and 31.0 kcal/mol of SiH_3 and F alone, respectively. The product **29a** with both substituents is 11.9 kcal/mol less favorable than the reactant, as compared to a predicted value of 6.4 kcal/mol, if the effects of F and SiH_3 alone are additive. Thus for the substrate with both SiH_3 and F groups both the barrier and product stability are much closer to those for the destabilizing F group alone.

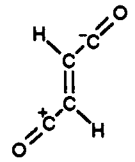
The calculated entropy changes for the ring openings are all positive, and range from 2.9 eu for the (SiH_3, SiH_3) substituted derivative **18** to 7.5 and 7.0 eu for the (H, H) and (F, F) derivatives **2** and **17**, respectively. An experimental value of 8.5 (±3.2) eu has been measured for 3-(trimethylsilyl)-4-phenylcyclobutenedione.[1d] The enthalpy changes are positive for the cyclobutenedione ring openings except for the (SiH_3, H) and (SiH_3, SiH_3) substituted compounds **16** and **18**, and so both ΔH and ΔS contribute to the favorable ΔG for these latter two compounds. The values of ΔH^{*} are similar to the values of E_a already discussed, and the values of ΔS^{*} are all rather small in magnitude, consistent with fairly modest net geometrical changes in the transition states. The experimental value for the formation of **3** (eq 3) is also small (0.2 ± 0.4 cal mol^{-1} K^{-1}),[1c] in good agreement with the calculated values.

Structures

The effects of the substituents on the intraring bond lengths and bond angles of the cyclobutenedione reactants and transition structures at the HF/6-31G* level are summarized in Table 4. The fluorines tend to cause a shortening of all of the intraring bonds in the reactants, with the largest effect on the C_3C_4 bond between the carbonyl carbons. The SiH_3-substituted derivatives show a very small decrease in the C_3C_4 bond length, and small increases in the others. The three transition structures with fluorine substituents all have a significantly greater elongation of the C_3C_4 bond in the transition structure compared to the unsubstituted derivative, by 0.039 to 0.073 Å, whereas the structures with the (SiH_3, H) and (SiH_3, SiH_3) substituents show smaller elongations of 0.016 and 0.042 Å of the C_3C_4 bond compared to the unsubstituted case. The changes in the C_1C_2 bond lengths reflect the same trends as those in C_3C_4 bonds, but are much less, and the C_1C_4 and C_2C_3 bond lengths all decrease by rather similar amounts. The transition structures for the three fluorinated molecules all have more product-like geometries, compared to the (SiH_3, H) and (SiH_3, SiH_3) substituted compounds, but as noted above the effects on the barriers are small for fluorine and larger for SiH_3.

Even though the fluorinated transition structures have greater elongation of the C_3C_4 bond, the $C_4C_1C_2C_3$ dihedral angles of 21.9°, 20.2°, and 23.5° for the (F, H), (F, F), and (F, SiH_3) derivatives, respectively, are less than that of 24.4° for the unsubstituted compound, while the dihedral angles in the (SiH_3, H), and (SiH_3, SiH_3) substituted transition structures of 25.9° and 27.8°, respectively, are greater. The $C_1C_2C_3$ or $C_2C_1C_4$ bond angles in the transition structures in which the central carbon is fluorine substituted are 105.0°, 103.6°, and 106.3° for the (F, H)-, (F, F)-, and (SiH_3, F)-substituted derivatives, and are greater, or more product-like, than the value for 101.9° for the (H, H)-substituted derivative. When the central carbon in the transition structure is substituted with SiH_3, the corresponding angles are 99.3°, 99,8°, and 99.0° for the (SiH_3, H), (SiH_3, SiH_3), and (SiH_3, F) derivatives, and are less, or more reactant-like, than that for the (H, H)-substituted parent. The relative sizes of these angles also reflect the corresponding angles in the product bisketene, which are 120.7°, 119.5°, and 121.3° for H substitution in the (H, H)-, (F, H)-, and (SiH_3, H)-substituted compounds, respectively; 122.6°, 121.0°, and 123.4° for F substitution in the (F, H)-, (F, F)-, and (SiH_3, F)-substituted compounds, respectively, and 118.0°, 118.2°, and 116.8° for SiH_3 substitution in the (SiH_3, H)-, (SiH_3, SiH_3)-, and (SiH_3, F)-substituted compounds, respectively.

In the cases examined (Table 4) the twisted bisketenes are found to be significantly more stable than the planar forms, in contrast to the situation with 1,3-butadiene,[2a] vinylketene, formylketene,[2e] and imidoylketene.[2e] This result is understandable by consideration of the expected lack of stabilization in the dipolar planar delocalized structure of bisketene **1**, which involves unfavorable acyl anion character (**1d**). The high negative charge density at the two central carbons of **1** would also destabilize planar structures. For the substituted bisketenes the coplanar structures would be further destabilized by steric interactions. The importance of nonplanar structures has been confirmed by photoelectron and dipole moment studies of bisketene **3**,[1f] and for silylated 1,3-butadienes.[10f] Even for 1,3-butadiene the *anti*-planar conformation is only 5.68 kcal/mol more stable than the 90° twisted geometry,[2a] and the destabilizing influences noted for the bisketene overcome this preference for coplanarity.



1d

In summary the results indicate that for these substituents the influence of the substituents on the ketenyl moiety is not the only effect on the cyclobutenedione ring opening, but ground state effects are important as well. The barriers for cyclobutenedione and cyclobutene ring opening are higher than that for cyclobutenone because of dipolar character in the transition state for the latter. Fluoro substituents are strongly destabilizing for the product bisketene, but the effects on the barriers for ring opening are much less because of the ground state destabilization. Silyl substituents stabilize the bisketene, and the barriers for ring opening are reduced by one-third the amount of this stabilization. These effects of substituents on the barriers and energy changes in these reactions are testable experimentally, and efforts in this direction are underway.

Acknowledgment. Financial support by the Natural Sciences and Engineering Research Council of Canada and helpful comments from Prof. K. Houk are gratefully acknowledged.

Supplementary Material Available: Tables of bond distances and angles (9 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

---

[10] (a) Lambert, J. B. *Tetrahedron* **1990**, *46*, 2677–2689. (b) White, J. C.; Cave, R. J.; Davidson, E. R. *J. Am. Chem. Soc.* **1988**, *110*, 6308–6314. (c) Siehl, H.-U.; Kaufmann, F.-P. *J. Am. Chem. Soc.* **1992**, *114*, 4937–4939. (d) Prakash, G. K. S.; Reddy, V. P.; Rasul, G.; Casanova, J.; Olah, G. A. *J. Am. Chem. Soc.* **1992**, *114*, 3076–3078. (e) Lambert, J. B.; Emblidge, R. W.; Malany, S. *J. Am. Chem. Soc.* **1993**, *115*, 1317–1320. (f) Bock, H.; Seidl, H. *J. Am. Chem. Soc.* **1968**, *90*, 5694–5700.