J. Org. Chem. **1996,** *61,* 2517−2522

Theoretical Predictions of Substituent Effects on the Thermal Electrocyclic Ring Openings of Cyclobutenones

Satomi Niwayama, E. Adam Kallel, Chimin Sheu, and K. N. Houk*

Department of Chemistry and Biochemistry, University of California, Los Angeles, California, 90095

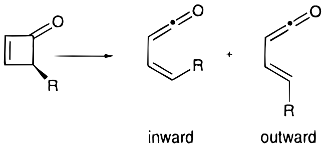
Received May 15, 1995 (Revised Manuscript Received January 24, 1996⊗)

The transition structures for the electrocyclic ring openings of a variety of substituted cyclobutenones were located with ab initio molecular orbital theory. The effects of substituents on the stereochemistries and activation energies of the electrocyclic ring openings are predicted to be similar to those in cyclobutene.

Introduction

The effect of substituents on the direction of conrotation in electrocyclic reactions was first explained by Kirmse, Rondan, and Houk in 1985 for the cyclobutene ring opening.[1a] The theory has been elaborated and verified experimentally for a number of reactions of cyclobutenes.[1] Since then the theory of stereoelectronic control of the direction of twisting of the breaking bond (torquoselectivity) has been extended to the pentadienyl cation cyclization,[2] the hexatriene−cyclohexadiene interconversion,[3a] the octatetraene−cyclooctatriene interconversion,[3b] the electrocyclic ring openings of azetines, oxetenes, and thietenes,[4] the ring opening of cyclopropenes,[5] and the electrocyclic openings of aziridines and oxiranes,[6] as well as cyclopentenyl anions.[7] This theory has also been applied to understand ground state distortions of cyclobutenes caused by substituents.[4,8] Here, we report a theoretical study of the electrocyclic ring openings of substituted cyclobutenones.

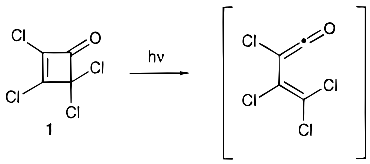
A substituent may rotate either inward or outward in the electrocyclic ring opening of cyclobutenones as shown.



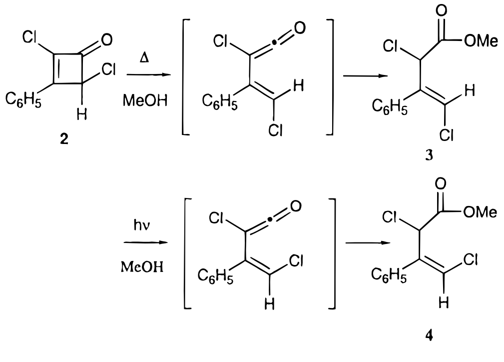
Our theoretical study was designed to establish the effect of substituents on the activation energies and stereochemistries of these processes.

Background

In 1968 Chapman and Lassila obtained spectroscopic evidence for the formation of substituted vinylketenes from photolysis of perchlorocyclobutenone, **1**.[9]



Later that year, Baldwin and McDaniel studied the thermal and photochemical reactions of 2,4-dichloro-3-phenylcyclobutenone, **2**.[10] The vinylketene intermediate was trapped by nucleophilic addition of methanol. The ester obtained in the thermal reaction is *E* alkene **3**, resulting from outward rotation of the chlorine. The photochemical reaction gave *Z* alkene **4** by inward rotation of the chlorine. Since the thermal electrocyclic reaction is readily reversible, the stereochemistries of these intermediates were determined from the trapping products.



Moore[11] and Liebeskind[12] independently showed that 1,4-quinones can be synthesized from aryl-, vinyl-, and

---

⊗ Abstract published in *Advance ACS Abstracts,* March 1, 1996.

[1] (a) Kirmse, W.; Rondan, N. G.; Houk, K. N. *J. Am. Chem. Soc.* **1984**, *106*, 7989. (b) Rondan, N. G.; Houk, K. N. *J. Am. Chem. Soc.* **1985**, *107*, 2099. (c) Rudolf, K.; Spellmeyer, D. C.; Houk, K. N. *J. Org. Chem.* **1987**, *52*, 3708. (d) Buda, A. B.; Wang, Y.; Houk, K. N. *J. Org. Chem.* **1989**, *54*, 2264. (e) Niwayama, S.; Houk, K. N. *Tetrahedron Lett.* **1992**, *33*, 883. (f) Niwayama, S.; Houk, K. N. *Tetrahedron Lett.* **1993**, *34*, 1251. (g) Niwayama, S.; Houk, K. N.; Kusumi, T. *Tetrahedron Lett.* **1994**, *35*, 527. (h) Hays, R.; Ingham, S.; Saengchantara, S. T.; Wallace. T. W. *Tetrahedron Lett.* **1991**, *32*, 2953.

[2] (a) Kallel, E. A.; Houk, K. N. *J. Org. Chem.* **1989**, *54*, 6006. (b) Smith, D. A.; Ulmer, C. W. *J. Org. Chem.* **1993**, *58*, 4118. (c) Smith, D. A.; Ulmer, C. W. *J. Org. Chem.* **1991**, *56*, 4444. (d) Smith, D. A.; Ulmer, C. W. *Tetrahedron Lett.* **1991**, *32*, 725.

[3] (a) Evanseck, J. D.; Thomas, B. E.; Spellmeyer, D. C.; Houk, K. N. *J. Org. Chem.* **1995**, *60*, 7134. (b) Thomas, B. E.; Evanseck, J. D.; Houk, K. N. *J. Am. Chem. Soc.* **1993**, *115*, 4165.

[4] Kallel, E. A. Ph.D. Dissertation, 1991, University of California, Los Angeles.

[5] Evanseck, J. D. Ph.D. Dissertation, 1990, University of California, Los Angeles.

[6] Nakamura, K.; Houk, K. N. *Heterocycles* **1993**, *35*, 631.

[7] Finocchio, A. L.; Tezuka, H.; Evanseck, J. D.; Houk, K. N. Unpublished results.

[8] (a) Spellmeyer, D. C.; Houk, K. N. *J. Am. Chem. Soc.* **1988**, *110*, 3412. (b) Niwayama, S.; Kallel, E. A.; Spellmeyer, D. C.; Sheu, C.; Houk, K. N. *J. Org. Chem.* In press.

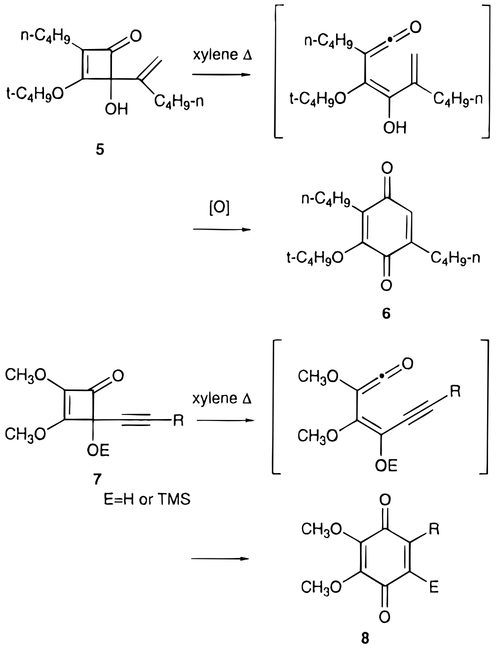
[9] Chapman, O. L.; Lassila, H. M. *J. Am. Chem. Soc.* **1968**, *90*, 2449.

[10] Baldwin, J. E.; McDaniel, B. L. *J. Am. Chem. Soc.* **1968**, *90*, 6118.

[11] (a) Gayo, L. M.; Winters, M. P.; Moore, H. W. *J. Org. Chem.* **1992**, *57*, 6896. (b) Ezcurra, J. E.; Pham, C.; Moore, H. W. *J. Org. Chem.* **1992**, *57*, 4787. (c) Xia, H. J.; Moore, H. W. *J. Org. Chem.* **1992**, *57*, 3765. (d) Xu, S. L.; Moore. H. W. *J. Org. Chem.* **1992**, *57*, 326. (e) Xu, S. L.; Taing, M.; Moore, H. W. *J. Org. Chem.* **1991**, *56*, 6104. (f) Reed, M. W.; Pollart, D. J.; Perri, S. T.; Foland, L. D.; Moore, H. W. *J. Org. Chem.* **1988**, *53*, 2477. (g) Xu, S. L.; Moore, H. W. *J. Org. Chem.* **1989**, *54*, 6018. (h) Xu, S. L.; Xia, H.; Moore, H. W. *J. Org. Chem.* **1991**, *56*, 6094. (i) Lee, K.; Moore, H. W. *Tetrahedron Lett.* **1993**, *34*, 235.

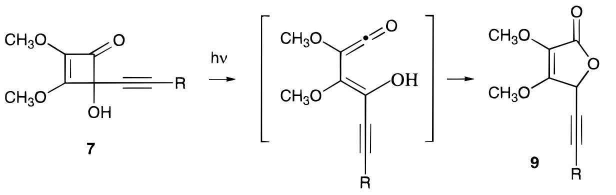
0022-3263/96/1961-2517$12.00/0

alkynyl-substituted cyclobutenones upon mild thermolysis as shown.



The reactions involve inward rotation of the vinyl and ethynyl groups so that cyclization is possible. Hydroxy is a more powerful electron-donating group than any of the unsaturated substituents listed above. From the earlier consideration of substituent effects in cyclobutene openings, the hydroxy group is expected to rotate outward during the ring opening.[1] However, the final product might arise from trapping of the intermediate in an equilibrating mixture, unless trapping is very fast.

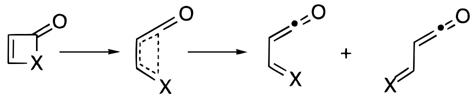
Moore and co-workers observed a reversal of torquoselectivity in the photochemical openings of cyclobutenones. Photolysis of **7** produced only butenolides **9** and no quinones **8**.



The photoproduct is derived by nucleophilic attack of the inward-rotating hydroxyl group on the ketene moiety formed in the reaction.[13] Moore has also extended this work to the synthesis of a wide range of annulated quinones.[14]

Nguyen, Ha, and More O'Ferrall[15] carried out theoretical studies of the electrocyclic reactions of cyclobutenone, azetenone, and oxetenone to form vinylketene, imidoylketene, and formylketene. They used the 6-31G** basis set, and the energies were determined at the MP2, MP3, and MP4 levels as well. The activation energies for these electrocyclic reactions decrease in the order of cyclobutenone, azetenone, and oxetenone (Table 1). *trans*-Vinylketene is more stable than *cis*-vinylketene by 1.6–1.8 kcal/mol at all the theory levels. They also noted that the thermal rearrangement of cyclobutenone is energetically less favorable than that of cyclobutene by ca. 6–8 kcal/mol.[8a] The cyclobutenone ring-opening reaction is nearly thermoneutral, consistent with its reversibility.

Table 1. MP2/6-31G//HF/6-31G** Energies (kcal/mol) of Electrocyclic Ring Openings[15]**



X= CH_2	0.0	28.2	1.0	-0.6
NH	0.0	12.5	-10.0	-9.9
O	0.0	1.3	-18.0	-17.5

Table 2. Activation Energies (kcal/mol) for Electrocyclic Reactions of Cyclobutene, Cyclobutenone and Cyclobutenediones[16]

compounds	HF/6-31G*// HF/6-31G*+ ZPE	MP2/G-31G*// HF/6-31G*+ ZPE	MP2/6-31G*// MP2/6-31G*+ ZPE
cyclobutene	45.2	35.7	35.8
cyclobutenone	37.8	26.7	26.7
cyclobutenedione	46.3	30.2	30.8

McAllister and Tidwell performed ab initio molecular orbital calculations on the ring opening of cyclobutenediones.[16] The ring openings of cyclobutene and cyclobutenone were also examined. Their calculations indicate that the ring opening of cyclobutenone has the lowest activation energy in this series (Table 2).

Computational Methods

All calculations were performed with Pople's GAUSSIAN 92 program.[17] All geometry optimizations were carried out at the RHF/6-31G* level of theory. Harmonic vibrational frequency calculations were performed on all stationary points. Single-point calculations were carried out using second-order Møller–Plesset theory(MP2) and the 6-31G* basis set on the RHF/6-31G*-optimized geometries. Zero-point energy corrections were made with 6-31G* frequencies scaled by 0.9.

Results and Discussion

Thermal Electrocyclic Opening of Cyclobutenone. In order to compare the results for the parent cyclobutenone system with those of substituted cases, cyclobutenone, the electrocyclization transition structure, and the product (vinylketene in s-*cis* and s-*trans* conformations) were located. Single-point calculations were performed at the MP2 level. Although the same calculations have been conducted at higher theory levels,[15] we employed this theory level for the other substituted cyclobutenones described in this paper. The geometries

---

(12) (a) Liebeskind, L. S.; Bombrun, A. *J. Org. Chem.* **1994**, *59*, 1149. (b) Edward, J. P.; Krysan, D. J.; Liebeskind, L. S. *J. Am. Chem. Soc.* **1993**, *115*, 9868. (c) Gurski, A.; Liebeskind, L. S. *J. Am. Chem. Soc.* **1993**, *115*, 6101. (d) Liebeskind, L. S.; Fengl, R. W.; Wirtz, K. R.; Shawe, T. T. *J. Org. Chem.* **1988**, *53*, 2482. (e) Liebeskind, L. S.; Granberg, K. L.; Zhang, J. J. *J. Org. Chem.* **1992**, *57*, 4345. (f) Krysan, D. J.; Gurski, A.; Liebeskind, L. S. *J. Am. Chem. Soc.* **1992**, *114*, 1412. (g) Liebeskind, L. S.; Wang, J. J. *J. Org. Chem.* **1993**, *58*, 3550.

(13) Foland, L. D.; Karlsson, J. O.; Perri, S. T.; Schwabe, R.; Xu, S. L.; Patil, S.; Moore, H. W. *J. Am. Chem. Soc.* **1989**, *111*, 979.

(14) (a) Foland, L. D.; Decker, O. H. W.; Moore, H. W. *J. Am. Chem. Soc.* **1989**, *111*, 989. (b) Enhsen, A.; Karabelas, K.; Heerding, J. M.; Moore, H. W. *J. Org. Chem.* **1990**, *55*, 1177.

(15) Nguyen, M. T.; Ha, T.-K.; More O'Ferrall, R. A. M. *J. Org. Chem.*, **1990**, *55*, 3251.

(16) McAllister, M. A.; Tidwell, T. T. *J. Am. Chem. Soc.* **1994**, *116*, 7233.

(17) GAUSSIAN 92. 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 Inc., Pittsburgh, PA, 1992.

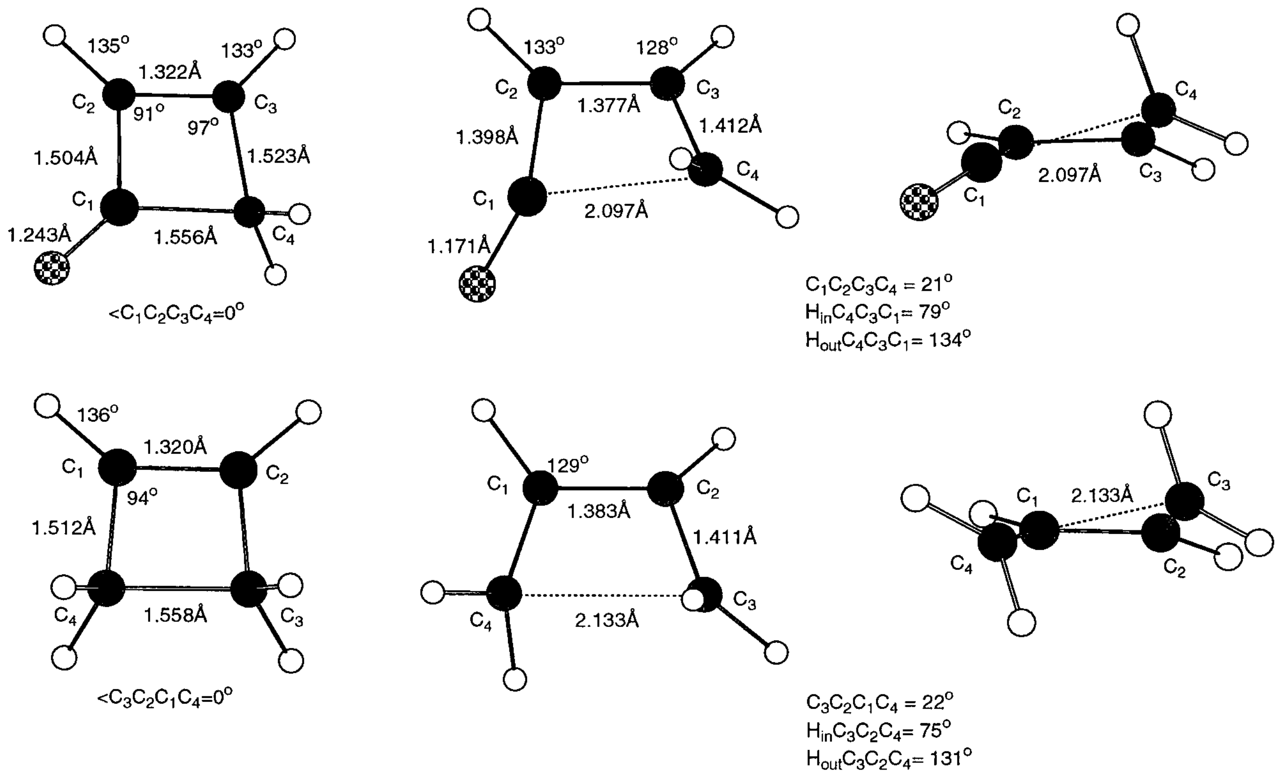


Figure 1. RHF/6-31G* geometries of reactants (left) and ring-opening transition structures (middle and right) for cyclobutenone (top) and cyclobutene (bottom).

Table 3. Relative Energies (kcal/mol) for the Cyclobutenone Electrocyclic Ring Opening

structure	RHF/3-21G+ZPE	RHF/6-31G*+ZPE[16]	MP2/6-31G*//6-31G*+ZPE[16]	MP2/6-31G**//RHF/6-31G**+ZPE[15]
ground state	0.0	0.0	0.0	0.0
transition structure	34.5	37.8	26.7	28.2
vinylketene (s-*cis*)	−9.5	−0.3	1.2	1.0
vinylketene (s-*trans*)	−10.8	−3.3	−0.2	−0.6

are compared to those of the corresponding cyclobutene reaction in Figure 1.

Cyclobutenone in the ground state is planar, while the transition structure, like that of cyclobutene, is distinctly nonplanar. The imaginary harmonic vibrational frequency of the transition structure corresponds to stretching of the breaking C_1-C_4 bond with simultaneous rotation of the C_4 hydrogens. It is not strictly proper to classify the reaction as conrotatory, since only one of the termini involved in bond breaking can give detectable rotation. Nevertheless, the transition state geometry is very similar to that of the transition state for the conrotatory cyclobutene opening. The breaking C−C bond is slightly shorter in the cyclobutenone transition structure (2.097 Å) than in the cyclobutene transition structure (2.133 Å). Since the C−C bonds which break are almost identical in length in the ground states, the ring opening of cyclobutenone has a slightly earlier transition state. As shown in Figure 1, the dihedral angles of the rotating hydrogens are nearly identical to the values for cyclobutene. The dihedral $HC_4C_3C_1$ is −79° for the inward-rotating hydrogen and 134° for the outward-rotating hydrogen of cyclobutenone. These values are −75° and 132°, respectively, for cyclobutene.

The energies of these stationary points are listed in Table 3 along with the result by Nguyen et al.[15] The activation energy is 9.0 kcal/mol lower for the cyclobutenone ring opening than for the cyclobutene opening at the MP2/6-31G*//6-31G* level. The experimental activation energy for the thermal reaction has not been reported. Since the activation energy of 34.5 ± 0.5 kcal/mol is known for the cyclobutene opening, the cyclobutenone opening should have an activation energy of about 25.5 kcal/mol. At the RHF/6-31G* level, the reaction is predicted to be exothermic by 3.3 kcal/mol. The MP2/6-31G*//6-31G* energies predict it to be exothermic by only 0.2 kcal/mol.

Substituent Effects on the Thermal Ring Opening. Transition structures were calculated for reactions of cyclobutenones with substituents at the 4 position. Amino, hydroxyl, fluoro, methyl, ethynyl, formyl, nitroso, and boryl groups were studied. This series of substituents covers a wide range of substituents from strong electron donor to strong electron acceptor. Amino, hydroxy, formyl, nitroso, and boryl cyclobutenones have two or three possible conformations with respect to the substituents. We located each transition structure or optimized each ground state structure and calculated the activation energies from the most stable conformers for each cyclobutenone. Table 4 shows the MP2/6-31G*//RHF/6-31G*+ZPE activation energies for the various substituted cyclobutenones and the deviation of those activation energies from the cyclobutenone activation energy. Table 4 also compares these substituent effects with those calculated for cyclobutene. The best available values from this work for cyclobutenones are compared to earlier work for cyclobutenes done at the RHF/6-31G*//3-21G theory level.[1,8] Some of them were also studied at the MP2/6-31G*//3-21G level; these values are quite similar and are listed in parentheses.

We define a relative energy (E_{in-out}) as the difference between the activation energy for a substituent rotating

Table 4. Relative Activation Energies (kcal/mol) for 4-Substituted Cyclobutenones (MP2/6-31G*//6-31G*+ZPE) and 3-Substituted Cyclobutenes (HF/6-31G*//3-21G (and MP2/6-31G*//3-21G+ZPE))[8b]

	cyclobutenone					cyclobutene		
substituent	$E_{a(in)}$	$\Delta E_{a(in)}$	$E_{a(out)}$	$\Delta E_{a(out)}$	$\Delta E_{a(in)} - \Delta E_{a(out)}$	$\Delta E_{a(in)}$	$\Delta E_{a(out)}$	$\Delta E_{a(in)} - \Delta E_{a(out)}$
NH_2	32.8	6.1	20.5	−6.2	12.3	6.0	−11.5	17.5
OH	34.0	7.3	21.5	−5.2	12.5	8.4	−8.8	17.2
F	35.1	8.4	23.2	−3.5	11.9	12.7 (9.1)	−4.2 (−6.2)	16.9 (15.3)
CCH	25.5	−1.2	20.3	−6.4	5.2	2.0	1.1	0.9
CH_3	29.8	3.1	23.3	−3.4	6.5	5.1 (3.6)	−1.7 (−1.7)	6.8 (5.3)
H	26.7	0.0	26.7	0.0	0.0	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)
NO	12.7	−14.0	17.6	−9.1	−4.9	−7.1 (−8.7)	−4.5 (−4.0)	−2.6 (−4.7)
CHO	15.8	−10.9	18.2	−8.5	−2.4	−8.2 (−10.1)	−3.6 (−5.4)	−4.6 (−4.7)
BH_2	5.5	−21.2	16.9	−9.8	−11.4	−25.4 (−24.4)	−7.2 (−5.7)	−18.2 (−18.7)

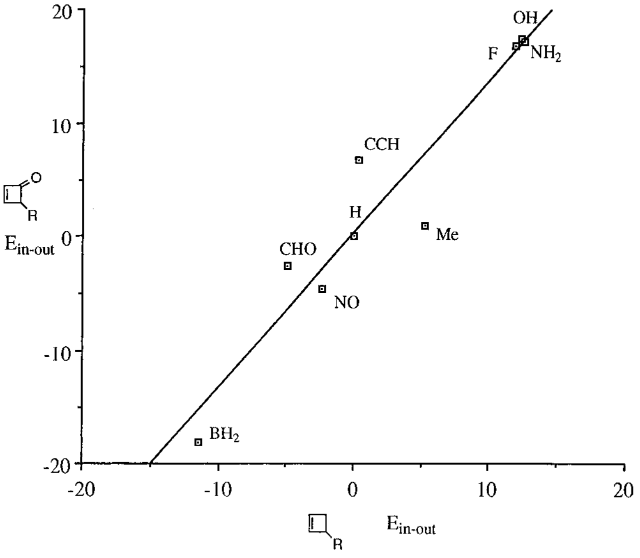


Figure 2. Plot of differences between inward and outward activation energies (kcal/mol) for cyclobutenones (MP2/6-31G*G//6-31G*) vs cyclobutenes (MP2/6-31G*//3-21G).

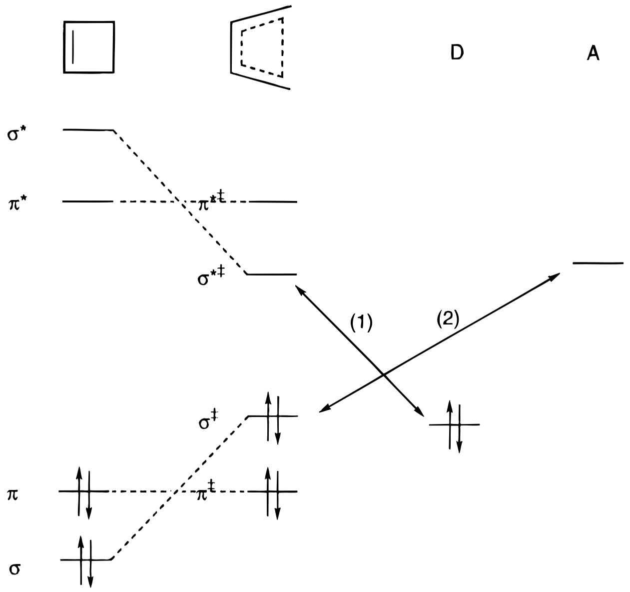


Figure 3. Frontier orbital energies of cyclobutene and transition state of cyclobutene ring opening. (1) Stabilizing interaction between $\sigma^{*\ddagger}$ and donor (D) HOMO. (2) Stabilizing interaction between $\sigma^{\ddagger}$ and acceptor (A) LUMO.

inward and the activation energy for that substituent rotating outward. These values for cyclobutenones and cyclobutenes are plotted in Figure 2.

We first examine the influence of substituents on the activation energies for outward rotation. In Table 4, it can be seen that donors lower the activation energy of outward rotation. The effect on cyclobutenones is much less than that on cyclobutenes. We have rationalized the substituent effects on the transition state of 3-substituted cyclobutene ring openings on the basis of the orbital interactions shown in Figure 3.

In the transition state for ring opening, the high-lying electron-donor orbital of the substituent (D) mixes with the low-lying $\sigma^{*\ddagger}$ LUMO of the breaking bond (Figure 3). This results in stabilization and lowering of the activation energy. Figure 4 compares the frontier orbitals of the transition states of the cyclobutene and cyclobutenone ring openings. The $\sigma^{*\ddagger}$ vacant orbital of the cyclobutenone transition state is higher in energy than the $\sigma^{*\ddagger}$ orbital of the cyclobutene transition state and is actually the SLUMO. Consequently, strong donors have a smaller energy-lowering effect in the cyclobutenone reaction than in the cyclobutene reaction.

The effect of acceptors is also smaller for outward rotation in cyclobutenone than for that in cyclobutenes. In the transition state, an acceptor vacant orbital can interact with the high-lying $\sigma^{\ddagger}$ orbital of the breaking bond (Figure 3). The HOMO of the cyclobutenone transition state is higher in energy than that of cyclobutene, but the coefficient at C_4 is relatively small (Figure 4). Consequently, the effect of donors and acceptors upon outward rotation is somewhat erratic relative to that of cyclobutenes. However, the difference between the activation energies for inward and outward rotation is linearly related to that found for cyclobutenes (Figure 2).

The reaction of substituted cyclobutenones represent another example of substituent control of torquoselectivity. The transition state orbitals shown in Figure 5 can be used to understand how this occurs. Upon inward rotation, the filled substituent donor orbital overlaps with the HOMO of the cyclobutenone transition state; this orbital is localized primarily on the breaking $C_3{-}C_4$ σ bond. This overlap results in a destabilizing cyclic four-electron interaction, which substantially raises the activation energy for the inward conrotation of a donor substituent. The interaction with the σ^* orbital of the breaking bond is very small. Conversely, outward rotation of a donor substituent lowers the activation energy substantially due to overlap of the donor substituent with the LUMO of the transition state (the breaking $C_3{-}C_4$ σ^* anti-bonding orbital). The overlap of the substituent donor orbital with the σ orbital is now small.

Acceptor substituents possess low-lying vacant orbitals, which upon inward rotation overlap strongly with the HOMO of the transition state. Outward conrotation of the acceptor substituent produces a smaller stabilizing effect, because of the smaller overlaps.

As noted earlier, the frontier orbitals of cyclobutenone provide an explanation of the altered torquoelectronic behavior of cyclobutenone compared to that of cy-

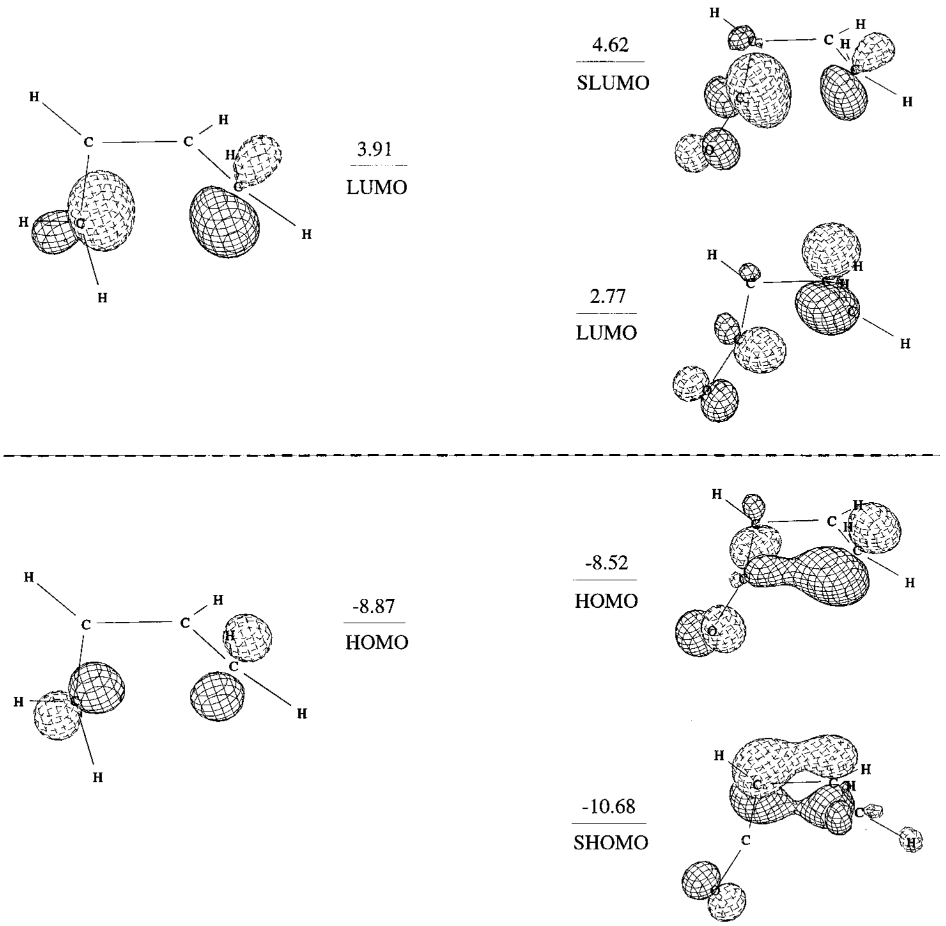


Figure 4. Frontier orbitals and energies (eV) for transition states of cyclobutene (left) and cyclobutenone (right) ring openings.

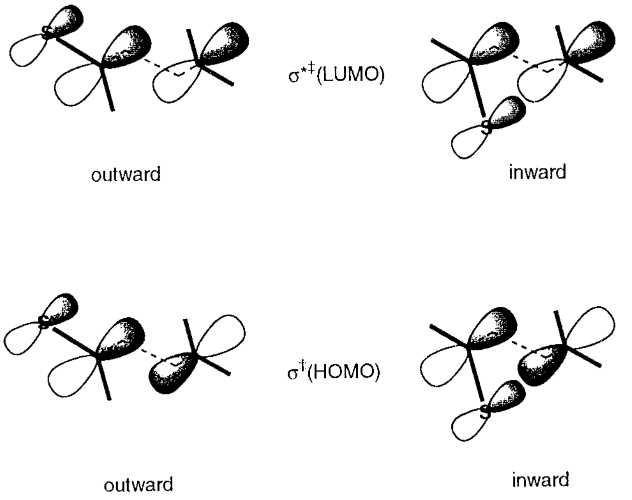


Figure 5. HOMO and LUMO of 4-substituted cyclobutenone transition states. Interaction with a substituent (S) p orbital rotating outward or inward.

clobutene. The SLUMO rather than the LUMO of the cyclobutenone transition state is mainly the C_1-C_4 antibonding orbital; the RHF/6-31G* energy is 4.62 eV, which is 0.71 eV higher in energy than the corresponding LUMO of cyclobutene. The cyclobutenone LUMO is lower than the cyclobutene LUMO, since it is a $\pi^*_{CC}-\pi^*_{CO}$ admixture, while a pure π^*_{CC} orbital is the SLUMO of cyclobutene. The HOMO corresponds to the breaking carbon−carbon bond mixed with the oxygen lone pair. The energy of this orbital is −8.52 eV. The corresponding orbital on cyclobutene has an energy of −8.87 eV. The σ and σ^* orbitals associated with the breaking CC bonds are lower in energy in the cyclobutene than in the cyclobutenone. This is a consequence of the electron-donating effect of the oxygen lone pair orbital in the cyclobutenone. The n orbital interacts in an antibonding fashion with σ_{14} and σ^*_{14}.

As in cyclobutene, $\Delta E_{\text{in-out}}$ displays an excellent correlation with the Taft $\sigma_R{}^0$ parameter.[18] Figure 6 is a plot of $E_{\text{in-out}}$ versus $\sigma_R{}^0$. This is in accord with the explanation of these substituent effects on the basis of the overlap of substituent π orbitals with the breaking σ bond orbitals.

The transition structures of 4-substituted cyclobutenone ring openings are very similar to each other and to the cyclobutenone transition state geometry (Table 5). The breaking C_1-C_4 bond length is 2.094 Å in cyclobutenone and varies from 2.057 Å with the inward-rotating 4-amino group to 2.136 Å for the inward-rotating 4-boryl group.

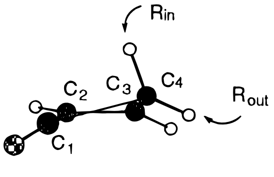
The results obtained are consistent with the experimental results described earlier. In particular, the preference for outward rotation of chlorine in the work of Baldwin[10] and for alkoxy or hydroxy in competition with alkyl or aryl[11,12] is fully consistent with the theoretical calculations. An example reported by Danheiser and Helgason[19] was believed to involve a cyclobutenone intermediate which is generated photochemically, but opens thermally to form **14**.

---

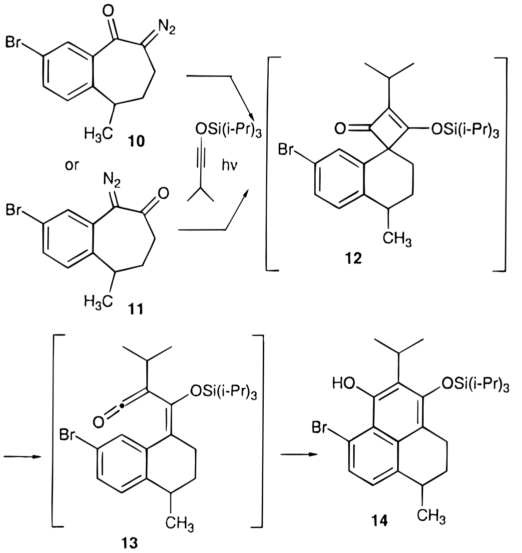
[18] Taft, R. W.; Lewis, I. C. *J. Am. Chem. Soc.* **1958**, *80*, 2436.

[19] Danheiser, R. L.; Helgason, A. L. *J. Am. Chem. Soc.* **1994**, *116*, 9471.

Table 5. Selected Geometrical Parameters of Transition Structures for Ring Openings



substituent (R)	stereochemistry	C_1-C_4	C_1-C_2	C_3-C_4	$\angle RC_4C_3C_1$	$\angle C_1C_2C_3C_4$
NH_2	R-in	2.057	1.373	1.405	91	29
	R-out	2.075	1.381	1.403	132	23
OH	R-in	2.061	1.376	1.406	86	30
	R-out	2.070	1.383	1.400	132	24
F	R-in	2.083	1.382	1.400	86	28
	R-out	2.069	1.383	1.392	132	24
CCH	R-in	2.122	1.394	1.422	83	21
	R-out	2.088	1.392	1.416	131	22
CH_3	R-in	2.077	1.379	1.404	84	24
	R-out	2.075	1.389	1.411	128	24
H		2.094	1.386	1.404	79	23
NO	R-in	2.110	1.410	1.433	77	18
	R-out	2.086	1.402	1.424	130	21
CHO	R-in	2.116	1.401	1.421	79	21
	R-out	2.121	1.398	1.425	131	20
BH_2	R-in	2.136	1.412	1.432	68	15
	R-out	2.110	1.404	1.438	124	18



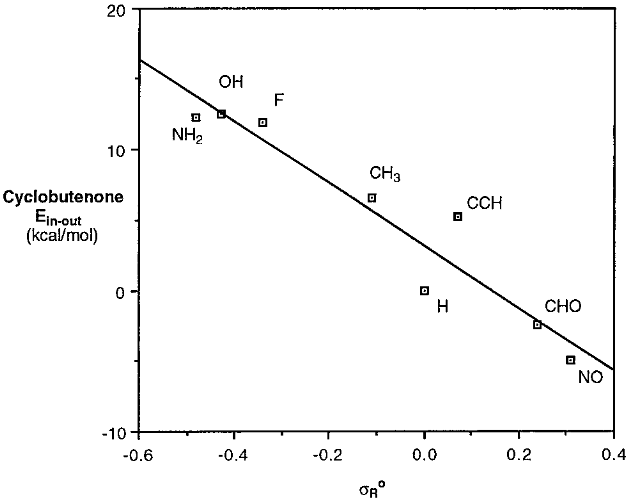


Figure 6. Plot of $E_{\text{in-out}}$ (kcal/mol, MP2/6-31G*//6-31G*) versus the Taft $\sigma_R{}^0$ for the thermal ring opening of 4-substituted cyclobutenones.

Our theory would predict outward rotation of the aromatic and inward rotation of the alkyl group, since the aryl group is a more powerful donor. This is opposite to the observed stereochemistry. It is possible that the thermal opening is readily reversible and eventually converts the kinetically favored isomer to the isomer **13**, which then cyclizes irreversibly to form **14**.[19]

Although we have not yet studied the origin of the reversed torquoselectivity in photochemical ring-opening reactions, a tentative rationalization of this selectivity can be made on the basis of previous studies of the excited state surface for this reaction. Kikuchi carried out MNDO/3-CI calculations on excited state reactions of cyclobutenones and predicted that the nπ* singlet excited state of cyclobutenone would open to a perpendicular diradical.[20] It is possible that substituents with lone pair groups prefer to rotate inward in order to interact in a stabilizing fashion with radical center at C_1 in the diradical. Further investigations of torquoselectivity in excited states are in progress.

Conclusion

The transition states for the electrocyclic ring openings of substituted cyclobutenones have been located. The transition structures are similar to those for the electrocyclic openings of cyclobutene. Substituent effects are smaller in the cyclobutenone case, due to the differing energies of the frontier molecular orbitals. The effects of substituents on the direction of ring opening are the same as in cyclobutenes.

Acknowledgment. We are grateful to the National Science Foundation for financial support of this work and to the San Diego Supercomputing Center and the UCLA Office of Academic Computing for computer time.

JO950899G

---

(20) Kikuchi, O. *Bull. Chem. Soc. Jpn.* **1982**, *55*, 1669.