

way to the enthalpies of formation of the protonated dicarbonyl compounds in the gas phase.

The heat of solution of methyl and ethyl iodides in Me_2SO are listed in Table IV. Since their heats of solution were small, the relative energies of the two systems are still very nearly what they were as reactants. The standard enthalpies of formation of both methyl and ethyl iodide in the liquid phase have been tabulated and are listed in Table IV. The enthalpies of formation of methyl and ethyl iodide differ by 7.26 kcal/mol, a normal value for methyl and ethyl homologues.

After completion of these processes, we have brought the alkylating agents out of solution and to their elemental constituents. In Figure 4 these two processes have been combined and are represented as the heats of formation of the alkylating agents in Me_2SO .

We are now left with solutions of potassium methylacetylacetonate and potassium ethylacetylacetonate in Me_2SO . The next two steps involve protonating the enolates and taking the resulting diketones out of solution to give the neat diketones and solutions of $\text{K}^+\text{Me}_2\text{SYL}^-$. Since the heats of deprotonation ΔH_D have previously been determined,⁶ heats of protonation are obtained by simply changing the sign for this value. After this correction, we are left with the relative enthalpies of hypothetical solutions of the undepronated β -diketones in $\text{K}^+\text{Me}_2\text{SYL}^-/\text{Me}_2\text{SO}$ solution. After subtracting the heats of solution of the diketones, which again are very similar, we are left with the neat β -diketones and $\text{K}^+\text{Me}_2\text{SYL}^-/\text{Me}_2\text{O}$ solutions. Since this solution is the same for both systems, we may neglect the enthalpy of the $\text{K}^+\text{Me}_2\text{SYL}^-$ solutions. Note that experimental determination of values for the heat of deprotonation involved by measuring the enthalpies for dissolving the neat diketones into a $\text{K}^+\text{Me}_2\text{SYL}^-/\text{Me}_2\text{SO}$ solution, which is exactly the reverse of what we have just accomplished in the previous two steps.

The enthalpies of vaporization and enthalpies of formation for methylacetylacetonate or ethylacetylacetonate have not been published. However, Irving and da Silva have measured enthalpies of vaporization for six closely related acyclic diketones and found an excellent correlation between these values and the boiling points of the compounds.²⁹ If one interpolates from the boiling points of methylacetylacetonate (bp 170–172 °C)³⁰ and ethylacetylacetonate

(bp 177–178 °C), values for their heats of vaporization of 11.9 and 12.3 kcal/mol, respectively, are obtained.

By summing up the columns in Table IV for both systems, the energies of ethylacetylacetonate and methylacetylacetonate relative to each other are calculated to be 3.13 kcal/mol. Since these are isomeric systems, they contain the same number and types of atoms, and this difference of 3.13 kcal/mol is equal to the difference of the heats of formation of the two β -dicarbonyl compounds in the gas phase. The value obtained is in good agreement with the average difference for heats of formation of methyl-substituted compounds as compared to their ethyl-substituted homologue²⁸ and serves as a check on the energy bookkeeping.

Conclusions

This paper and its predecessor⁶ provide an unusually detailed analysis of the effects of structure, temperature, and ion pairing on the thermodynamic stabilities and kinetic reactivities of some symmetrical enolate anions. Even for these greatly simplified systems, the effect of varying the conditions is complex and often not readily interpreted by us. For example the relative rates of two very similar reactions (ethylation of methylacetylacetonate and ethylacetylacetonate) are inverted above and below room temperature.

An apparently novel strategy (the method of isomeric pathways) for comparing clean reactions which give the same product permits an extensive comparison of many states of the reactants, products, and transition states on a common enthalpy scale.

The reactions of enolates constitute the largest family of processes in synthetic chemistry and have been fair game for ad hoc interpretations of even modest product differences in terms of stereoelectronic theories derived for isolated molecules in the gas paper. The occasionally complex relations of structure and reactivity reported here for carefully simplified systems provide a warning against the arbitrary and uncalled for interpretation of small differences in reactivity for base-promoted reactions of carbonyl compounds.

Acknowledgment. We are grateful for support of this work by NSF Grant CHE-8006202 to E.M.A., an N.I.H. Fellowship to G.W.S., and for the help of John Harrelson and helpful discussions with F. G. Bordwell.

Registry No. $\text{Li}^+\text{MeAcAc}^-$, 70902-15-7; $\text{Na}^+\text{MeAcAc}^-$, 34916-51-3; $\text{K}^+\text{MeAcAc}^-$, 72610-66-3; $\text{Li}^+\text{EtAcAc}^-$, 94904-86-6; $\text{Na}^+\text{EtAcAc}^-$, 18995-15-8; $\text{K}^+\text{EtAcAc}^-$, 94904-87-7; LiMDD, 22643-61-4; NaMDD, 17372-26-8; KMDD, 37892-21-0.

(30) Baumgarten, H. E., Ed. "Organic Synthesis"; Wiley: New York, 1973; Collect. Vol. 5, pages 785–786.

(28) (a) Pedley, J. B.; Rylance, J. "Sussex-NPL Computer Analyzed Thermochemical Data: Organic and Organometallic Compounds"; University of Sussex: Brighton, 1977. (b) Cox, J. D.; Pilcher, G. "Thermochemistry of Organic and Organometallic Compounds"; Academic Press: New York, 1970.

(29) Irving, R. J.; daSilva, A. V. R. *J. Chem. Soc., Dalton Trans.* 1975, 798.

Theory of Stereoselection in Conrotatory Electrocyclic Reactions of Substituted Cyclobutenes

Nelson G. Rondan* and K. N. Houk*

Contribution from the Department of Chemistry, University of Pittsburgh, Pittsburgh, Pennsylvania 15260. Received October 12, 1984

Abstract: Ab initio transition structures for the conrotatory electrocyclic ring openings of cyclobutene, *trans*-3,4-dimethylcyclobutene, and *trans*-3,4-dihydroxycyclobutene were computed using gradient techniques and the 3-21G basis set. For the disubstituted cyclobutenes, the transition structures leading to the *E,E* butadienes are more stable than those leading to the *Z,Z* isomer, consistent with the observed stereochemistries of related reactions. There is a very large preference for rotation of substituents "outward", which is shown to increase as the donor character of the substituent increases. Conventional steric effects are too small to explain these large effects. A theoretical rationale is provided to explain this effect and to predict the stereoselectivities of related reactions.

Cyclobutenes and butadienes interconvert thermally by a conrotatory process.^{1,2} Brauman and Golden estimated that the

allowed conrotatory process is 15.0 kcal/mol more favorable than the disrotatory process.³ Various theoretical treatments predict

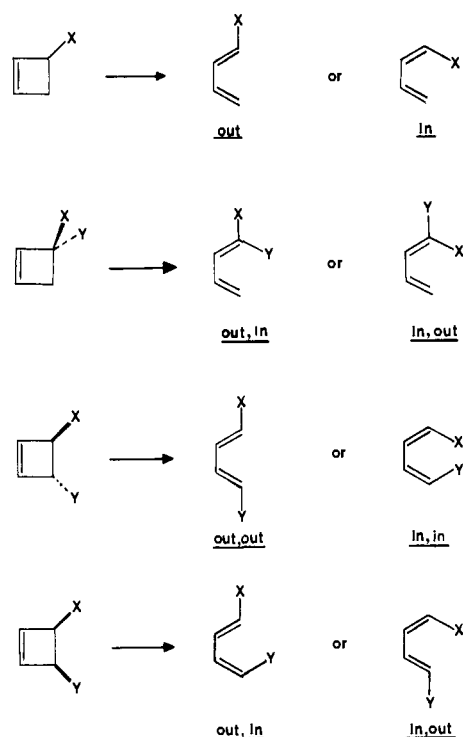


Figure 1. "Outward" (out) and "inward" (in) conrotatory processes for mono- and disubstituted cyclobutenes.

the favorability of the conrotatory process but differ markedly on the energetic difference between the two processes.⁴ Breulet and Schaefer recently reported calculations in accord with the experimental estimate.⁵ In substituted cases, substituents at C₃ or C₄ of cyclobutene may either rotate "inward" or "outward" during a conrotatory process. Because 3-substituted cyclobutenes generally form trans-substituted butadienes,^{6,7} it is frequently suggested that outward substituent rotation is preferred for steric reasons. However, there are ample data on 3,3-disubstituted and 3,4-disubstituted cyclobutenes which contradict this compellingly simple idea.⁸⁻¹¹ We have carried out theoretical studies of substituent effects on rates and stereoselectivities of conrotatory

Table I. Activation Energies of Conrotatory Electrocyclic Reactions of Cyclobutenes^{a-c,11}

	E_a (kcal/mol)	E_{rel} (kcal/mol)
cyclobutene ^d	32.5	0.0
3-methylcyclobutene ^b	31.6	-0.9
cis-3,4-dimethylcyclobutene ^c	34.0	+1.5
trans-3,4-dimethylcyclobutene	30.6	-1.9
3-chlorocyclobutene	29.4	-3.1
cis-3,4-dichlorocyclobutene	35.6	+3.1
trans-3,4-dichlorocyclobutene	25.7	-6.8
cis-3-chloro-4-methylcyclobutene ^d	31.6	-0.9
3-ethoxycyclobutene	23.5	-9.0
cis-3,4-diethoxycyclobutene	27.8	-4.7
cis-3,4-dimethoxycyclobutene	28.6	-3.9
cis-3-chloro-4-methoxycyclobutene ^e	29.1	-3.4
cis-3-methoxy-4-methylcyclobutene ^e	25.5	-7.0
3-acetoxycyclobutene	27.8	-4.7

^aCooper, W.; Walters, W. D. *J. Am. Chem. Soc.* **1958**, *80*, 4220.
^bFrey, H. M.; Marshall, D. C. *Trans. Faraday Soc.* **1965**, *61*, 1715.
^cSrinivasan, R. *J. Am. Chem. Soc.* **1969**, *91*, 7557. ^dCl rotates outward. ^eMeO rotates outward.

Table II. Substituent Effects on the Activation Energies for Conrotatory Electrocyclic Reactions of Cyclobutenes and Derivatives^a

substituents	"outward"	"inward"
CH ₃	-1	+3
Cl	-3	+6
OR	-9	+5
OAc	-5	

^aEstimated to be additive to within ± 1 kcal/mol for each substituent.

electrocyclizations of cyclobutenes. We have devised a theory which provides an understanding of experimental data and leads to a number of predictions for substituents not yet studied, as well as for other electrocyclic processes.

Background

For substituted cyclobutenes, there are two stereochemically distinct conrotatory processes, as depicted in Figure 1. A given substituent may either rotate "outward", leading to the *E* butadiene, or "inward", to give the *Z* butadiene. Early studies by Criegee, Winter, Frey, and their co-workers showed that alkyl substituents at C₃ preferentially rotate outward.⁶ For example, 3-methylcyclobutene gives only *trans*-piperylene, and *trans*-1,2,3,4-tetramethylcyclobutene gives only (*E,E*)-2,4-hexadiene. These and related results were rationalized on the basis of steric arguments. That is, although the inward rotations of the substituents are allowed by orbital symmetry, steric repulsions destabilize the corresponding transition states. Consequently, only the products resulting from outward rotations are observed.

In *cis*-disubstituted, 3,3,4-trisubstituted, and 3,3,4,4-tetrasubstituted cyclobutenes, one or two substituents must rotate inward in a conrotatory process. From experimental measurements of rates of such processes, it is possible to determine quantitatively the influence of inward rotations of substituents upon activation energies.

A systematic investigation by Frey and co-workers on the influence of methyl substituents on rates of reaction revealed that alkyl substituent effects at C₃ and C₄ are approximately additive.⁷ Kirmse obtained data on a wider range of substituents.¹¹ Data on representative cyclobutenes used to assess C₃ and C₄ substituent effects on the activation energies of the outward and inward rotations of substituted cyclobutenes are given in Table I.¹¹

Substituent effects on the activation energies for outward rotations were obtained from the differences between the activation energies for the reactions of the parent cyclobutene and 3-substituted cyclobutenes. For example, the activation energy of the reaction of 3-methylcyclobutene is 0.9 kcal/mol lower than that of cyclobutene, showing that methyl substitution at C₃ lowers the activation energy for outward rotation by about 1 kcal/mol.

(1) For a review on the electrocyclic reactions of cyclobutenes, see: Marvell, E. "Thermal Electrocyclic Reactions"; Academic Press: New York, 1980; pp 124-213.

(2) Woodward, R. B.; Hoffmann, R. "The Conservation of Orbital Symmetry"; Verlag Chemie International: Deerfield Beach, Fla, 1970.

(3) Brauman, J. I.; Golden, D. M. *J. Am. Chem. Soc.* **1968**, *90*, 1920.

(4) Filer, G. *Theor. Chim. Acta* **1968**, *12*, 412. Van der Lugt, W. Th. A. M.; Oosterhoff, L. J. *Chem. Commun.* **1968**, 1235. Van der Lugt, W. Th. A. M.; Oosterhoff, L. J. *J. Am. Chem. Soc.* **1969**, *91*, 6042. Dewar, M. J. S.; Kirschner, S. *Ibid.* **1971**, *93*, 4290-4292. Dewar, M. J. S.; Kirschner, S.; Kollmar, H. W. *Ibid.* **1974**, *96*, 5240. Dewar, M. J. S.; Kirschner, S. *Ibid.* **1974**, *96*, 6809. Hsu, K.; Buenker, R. J.; Peyerimhoff, S. D. *Ibid.* **1971**, *93*, 2117. Hsu, K.; Buenker, R. J.; Peyerimhoff, S. D. *Ibid.* **1972**, *94*, 5639. Buenker, R. J.; Peyerimhoff, S. D.; Hsu, K. *Ibid.* **1971**, *93*, 5005. McIver, J. W., Jr.; Komornicki, A. *Ibid.* **1972**, *94*, 2625. Rastelli, A.; Pozzoli, A. S.; Del Re, G. *J. Chem. Soc., Perkin Trans. 2* **1972**, 1571. Tee, O. S. *J. Am. Chem. Soc.* **1969**, *91*, 7144. Tee, O. S.; Yates, K. *Ibid.* **1972**, *94*, 3074.

(5) The most recent theoretical work on this subject was reported in: Breulet, J.; Schaefer, H. F., III *J. Am. Chem. Soc.* **1984**, *106*, 1221. Several substituent effects have also been calculated by MNDO: Jenson, A.; Kunz, A. *Theor. Chim. Acta* **1984**, *65*, 33.

(6) (a) Criegee, R.; Noll, K. *Justus Liebigs Ann. Chem.* **1959**, *627*, 1. Winter, R. E. K. *Tetrahedron Lett.* **1965**, 1207. Branton, G. B.; Frey, H. M.; Skinner, R. F. *Trans. Faraday Soc.* **1966**, *62*, 1546.

(7) Frey, H. M.; Pope, H. M.; Skinner, R. F. *Trans. Faraday Soc.* **1967**, *63*, 1166. Frey, H. M.; Solly, R. K. *Ibid.* **1969**, *65*, 448.

(8) Curry, M. J.; Stevens, I. D. R. *J. Chem. Soc., Perkin Trans. 2* **1980**, 1391.

(9) Arnold, B. J.; Sammes, P. G.; Wallace, T. W. *J. Chem. Soc., Perkin Trans. 1* **1974**, 409, 415.

(10) Dolbier, W. R.; Koroniak, H.; Burton, D. J.; Bailey, A. R.; Shaw, G. S.; Hansen, S. W. *J. Am. Chem. Soc.* **1984**, *106*, 1871.

(11) Kirmse, W.; Rondan, N. G.; Houk, K. N. *J. Am. Chem. Soc.* **1984**, *106*, 7989.

Substituent effects on the inward rotations were assessed from the differences between the activation energies for 3-substituted cyclobutenes and the corresponding *cis*-3,4-disubstituted derivatives. The reaction of *cis*-3,4-dimethylcyclobutene has a 2.5-kcal/mol higher activation energy than that of 3-methylcyclobutene, which is taken as a measure of the effect of inward rotation of a methyl substituent. Deductions made in this way are summarized in Table II. These values can be seen to predict the activation energies for the reactions of Table I within 1 kcal/mol. Substituents at C₃ and C₄ lower the activation energies for outward rotation, but increase the activation energies for inward rotation. Assuming additivity, the values in Table II can also be used to estimate the differences in activation energies between other conrotatory processes. For example, the double-outward transition state for the reaction of *trans*-3,4-dimethylcyclobutene is predicted to be $2[+3 - (-1)] = 8$ kcal/mol higher in energy than the double-inward transition state. For *trans*-3,4-dichloro and *trans*-3,4-dialkoxy cyclobutenes, the differences in activation energies are 18 and 28 kcal/mol, respectively.

The large differences in activation energies between the outward and inward rotations cannot all be due to steric effects. Thus, various measures of steric effects of substituents indicate that the size of substituents decreases in the order: CH₃ > OR ≈ Cl. For example, *A* values for these groups are 1.7, 0.7, and 0.4, respectively,^{12a} while Taft *E*_S values are -1.24, -0.55, and -0.97.^{12b} Clearly, some large electronic effect disfavors inward rotation of Cl or OR. In 1980, Curry and Stevens reported an extensive study of the electrocyclic reactions of 3-methyl-3-alkylcyclobutenes, and pointed out that steric effects do not have a significant influence on outward vs. inward rotation, since alkyl groups larger than methyl often rotate inward in preference to methyl.⁸ For 3-methyl-3-*R*-cyclobutenes, the ratio of *R*-inward to *R*-outward rotation is 2.1, 1.6, 0.8, 1.9, 0.5, and 0.5 for *R* = Et, *n*-Pr, *c*-Pr, *i*-Pr, *t*-Bu, and Ph, respectively, at 180 °C.⁸ Thus, ethyl, propyl, and isopropyl groups rotate inward in preference to methyl, while cyclopropyl, *tert*-butyl, and phenyl show a very small preference for outward rotation as compared to methyl. These authors proposed that since methyl is the poorest donor of the alkyls, the residual negative charge about methyl will experience more repulsion of C₄ upon inward rotation than will occur for better donor groups.⁸

Dolbier and co-workers recently reported an additional case that cannot be explained by steric arguments.¹⁰ These authors reported that *trans*-perfluoro-3,4-dimethylcyclobutene preferentially opens thermally to the *Z,Z* isomer, which involves inward rotation of both of the trifluoromethyl groups. The activation energy leading to the *E,E* isomer is 19.2 kcal/mol higher.¹⁰ If the reaction were controlled by steric effects, the *E,E* isomer would be the preferred product, since F is considerably smaller than CF₃. F and CF₃ have *E*_S parameters of -0.46 and -2.4, respectively.^{12b} By this measure, CF₃ is nearly as large as *t*-Bu (*E*_S = -2.78).^{12b}

Dolbier rationalized these results on the basis of the differences in the direction of the pyramidalizations of the olefinic carbons in the reactants.¹⁰ For example, in *trans*-1,2,3,4-tetramethylcyclobutene, the olefinic carbons are assumed to pyramidalize in such a way that the olefinic methyls rotate away from the methyl groups at C₃ and C₄, in analogy to pyramidalization calculated for other hydrocarbons.¹³ The direction of pyramidalization is assumed to dictate the direction of rotation of the substituents at C₃ and C₄. For *trans*-perfluorodimethylcyclobutene, the direction of pyramidalization is assumed to be opposite to that of tetramethylcyclobutene, and, therefore, opposite stereoselectivity is assumed to result.

Carpenter has devised a qualitative model for substituent effects upon pericyclic reactions rates.¹⁴ In his model, HMO calculations are performed on reactants and transition states, modeled as the

isoconjugate cyclic conjugated hydrocarbons. Carpenter's model does not take into account the stereochemistries of the type described here, and also does not differentiate between different types of donor, acceptor, or conjugating substituents. For cyclobutene conrotatory electrocyclic reactions, Carpenter's model predicts only that all types of substituents at C₃ or C₄ will accelerate the reaction.¹⁴

Epiotis has proposed that substituent effects on electrocyclic reactions may be treated by considering the electrocyclic closure of a butadiene as an intramolecular $\pi_2s + \pi_2a$ cycloaddition.¹⁵ The faster rate of reaction of 3-ethoxycyclobutene (*E*_a = 23.5 kcal/mol) than that of *cis*-3,4-diethoxycyclobutene (*E*_a = 27.8 kcal/mol) was interpreted as a result of the greater polarity of the former. This treatment overlooked the fact that one of the ethoxy groups must rotate inward in the latter molecule. Most indications are that C₃ and C₄ substituent effects are additive, as long as both groups rotate outward, so that the difference between the ionization potential of one alkene unit and the electron affinity of the other¹⁵ is not a generally valid index of reactivity.

What is the origin of the very large stereochemically dependent substituent effects observed upon electrocyclic reactions of cyclobutenes? In order to answer this question, we have located *ab initio* transition structures with the 3-21G basis set for the conrotatory electrocyclic openings of cyclobutene, *trans*-3,4-dimethylcyclobutene, and *trans*-3,4-dihydroxycyclobutene. We have also carried out single-point calculations on the influence of a variety of substituents on the activation energies and stereochemical preferences in such reactions. An explanation of substituent effects on rates and stereochemistries is developed, and predictions of stereochemistries of related reactions are made.

Theoretical Methods

Transition structures, reactants, and products were fully optimized with *ab initio* RHF calculations using the split-valence 3-21G basis set¹⁶ and gradient optimizations.¹⁷ In calculating the transition structures, a C₂ symmetry constraint was imposed, but for the parent system, the resulting maximum was proven to be a transition structure by the calculation of vibrational frequencies from analytical second derivatives.^{17b} The *trans*-disubstituted compounds were studied in order to take advantage of the C₂ symmetry of these molecules, which made the calculations faster than calculations on the analogous monosubstituted systems. The geometrical parameters and energetics of the reactants and the transition structures are summarized in Tables III and IV, respectively. The 3-21G vibrational frequencies of cyclobutene and butadiene were evaluated using analytical second-derivative techniques.^{17b} Single-point calculations with second-order correlation energy corrections (MP2/3-21G//3-21G) were carried out on cyclobutene and the transition structure. Single-point 3-21G calculations were carried out on a variety of model transition structures for other *trans*-3,4-disubstituted cyclobutenes. The geometries for these model calculations were derived from the cyclobutene transition structure by replacement of the methylene hydrogens by the substituents, using standard geometries¹⁸ for the latter.

Transition Structures for Conrotatory Electrocyclizations

Cyclobutene. During the course of this work, Breulet and Schaefer reported the transition structure for the conrotatory electrocyclic reaction of cyclobutene using a double- ζ (DZ) basis set and a two-configuration self-consistent-field (TCSCF) wave function.⁵ The split-valence basis set we have used is somewhat

(12) (a) Eliel, E. L.; Allinger, N. L.; Angyal, S. J.; Morrison, G. A. "Conformational Analysis"; Wiley: New York, 1965; p 44. (b) Unger, S. H.; Hansch, C. *Prog. Phys. Org. Chem.* **1976**, *12*, 91.

(13) Rondan, N. G.; Paddon-Row, M. N.; Caramella, P.; Houk, K. N. *J. Am. Chem. Soc.* **1981**, *103*, 2436.

(14) Carpenter, B. *Tetrahedron* **1978**, *34*, 1877.

(15) Epiotis, N. In "Rearrangements in Ground and Excited States"; de Mayo, P., Ed.; Academic Press: New York, 1980; pp 1-90.

(16) Binkley, J. S.; Pople, J. A.; Hehre, W. *J. Am. Chem. Soc.* **1980**, *102*, 939.

(17) (a) Binkley, J. S.; Whiteside, R. A.; Krishnan, R.; Seeger, R.; DeFrees, D. J.; Schlegel, H. B.; Topiol, S.; Kahn, L. R.; Pople, J. A. *GAUSSIAN 80*, Carnegie-Mellon University, Pittsburgh PA. (b) *GAUSSIAN 82*, implemented on the CMU VAX, was used for the analytical second derivative calculations.

(18) Pople, J. A.; Beveridge, D. L. "Approximate Molecular Orbital Theory"; McGraw-Hill: New York, 1970; p 111.

Table III. 3-21G Geometries and Energies of Cyclobutene, *trans*-3,4-Dimethylcyclobutene, and *trans*-3,4-Dihydroxycyclobutene

		3,4- dimethyl- cyclobutene	3,4- dihydroxy- cyclobutene
Bond Lengths, Å			
C ₁ C ₂	1.326	1.326	1.326
C ₂ C ₃	1.539	1.539	1.542
C ₃ C ₄	1.593	1.592	1.564
C ₁ H ₅	1.068	1.069	1.068
C ₃ H ₇	1.081	1.083	1.080
C ₃ C ₇		1.528	
C ₇ H ₁₁		1.086	
C ₇ H ₁₃		1.085	
C ₇ H ₁₅		1.084	
C ₃ O ₇			1.424
O ₇ H ₁₁			0.966
Bond Angles, Deg			
C ₁ C ₂ C ₃	95.0	95.0	94.3
C ₂ C ₃ C ₄	85.0	85.0	85.5
C ₂ C ₁ H ₅	133.3	133.4	133.3
C ₂ C ₃ H ₇	115.4	114.4	113.3
C ₂ C ₃ C ₇		115.5	
C ₇ C ₃ H ₁₁		110.9	
C ₃ C ₇ H ₁₂		110.9	
C ₃ C ₇ H ₁₃		110.1	
C ₂ C ₃ O ₇			118.8
C ₃ O ₇ H ₁₁			111.3
Dihedral Angles, Deg			
C ₁ C ₄ C ₃ C ₂	0.0	0.8	-4.5
C ₃ C ₄ C ₁ C ₂	0.0	-1.0	5.3
C ₄ C ₁ C ₂ C ₃	0.0	1.0	-5.4
H ₅ C ₁ C ₂ C ₄	180.0	179.2	179.3
H ₉ C ₃ C ₂ C ₁	-114.6	-113.6	-104.5
H ₅ C ₁ C ₇ H ₆	0.0	-0.7	-4.0
C ₇ C ₃ C ₂ C ₁		114.8	
H ₁₁ C ₇ C ₃ C ₂		71.5	
H ₁₃ C ₇ C ₃ C ₂		191.5	
H ₁₅ C ₇ C ₃ C ₂		-48.2	
O ₇ C ₃ C ₂ C ₁			119.1
H ₁₁ O ₇ C ₃ C ₂			87.4
α ^a		0.6	0.5
Energies (au)			
3-21G//3-21G	-154.03072	-231.67551	-302.89564
3-21G//3-21G + ZPE	-153.93768		
MP2/3-21G//3-21G	-154.38492		
MP2/6-31G**//3-21G	-155.40775		

^a α is the out-of-plane angle of the vinylic hydrogens obtained from the following equation: $\sin \alpha = \sin \angle H_5C_1C_2 \sin \angle H_9C_3C_2C_4$.

inferior to that of Schaefer, and our use of a single configuration does not allow for electron correlation, which should be especially important for the pair of electrons involved in the breaking bond. Nevertheless, the geometrical results we have obtained are similar to Schaefer's (see below), and the energies are comparable when the MP2 calculations are compared with Schaefer's TCSCF results.

Two views of the 3-21G transition structure for the ring opening of cyclobutene are shown in Figure 2. The geometry is summarized in Table IV, along with that from Breulet-Schaefer's DZ TCSCF calculation.⁵ The numbers in parentheses in Table IV signify the reaction progress, which we define as the percentage of change of that parameter from reactant to product, using the same type of calculation for reactants, transition structures, and products. For example, 0% reaction progress refers to the reactant geometry (cyclobutene), and 100% reaction progress corresponds to the product geometry (*cis*-butadiene). A planar structure of *s-cis*-butadiene was used for these comparisons, even though the cisoid species is nonplanar.¹⁹ We use the cyclobutene numbering

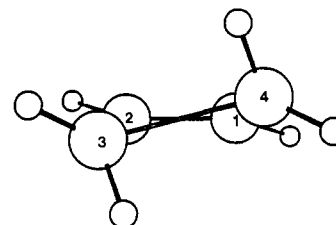
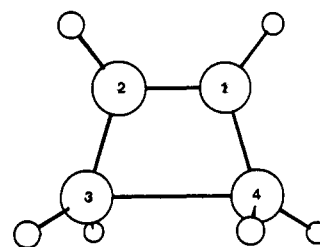


Figure 2. Two views of the 3-21G transition structure for the conrotatory cyclobutene-butadiene interconversion. Geometrical data are given in Table IV.

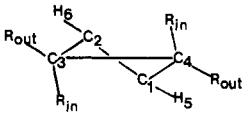
scheme in the following discussions.

In the transition structure, the breaking C₃C₄ bond length is 2.138 Å, corresponding to reaction progress of 37%. For comparison, the C₃C₄ bond length according to DZ TCSCF is 2.238 Å, or reaction progress of 43%. While the C₃C₄ bond length suggests that the DZ TCSCF transition structure is slightly more advanced ("later") than the 3-21G transition structure, the lengths of the incipient C₂C₃ and C₁C₄ double bonds suggest the opposite. According to the 3-21G results, the incipient double bonds are 54% formed, as compared to 39% for the DZ TCSCF transition structure. The most striking difference between the 3-21G and the DZ TCSCF transition structures is the C₁C₂ bond length. We predict that the C₁C₂ double bond, which becomes a single bond in the product, lengthens (28% reaction progress) in the transition structure, contrary to the shortening of this bond (-11% reaction progress) in the Breulet-Schaefer calculations.⁵ Most likely this discrepancy arises from the unusually long cyclobutene double-bond length in the TCSCF structure.

The bond angles are very similar in the transition structures obtained by the two methods. However, the dihedral angles are quite different. For example, the dihedral angle, $\angle H_5C_1C_2H_9$ is 31.5°, 14° larger than in the DZ TCSCF TS. This is a consequence of the greater tendency of the vinylic carbons to pyramidalize in the 3-21G TS. In the TCSCF TS, the C₁C₂ bond acquires more double-bond character, and there is consequently less tendency for the vinylic carbons to pyramidalize. The pyramidalizations of the vinylic carbons occur in order to maximize the overlap of the orbitals at C₁ and C₂ with the developing p orbitals at C₃ and C₄, since double-bond character is developing in the transition structure. The differences in magnitudes of the other torsion angles involving the vinylic hydrogens are merely due to the greater distortions of the vinylic hydrogens away from planarity in the 3-21G TS.

The methylene termini are rotated by 42.9°, equivalent to 48% reaction progress. The magnitude of the rotation of the methylene termini is defined as the dihedral angle BC₄C₁C₂, where B is the bisector of the H_{out}-CH_{in} angle. To summarize, the reaction progress of the 3-21G TS ranges from 28 to 54% while the reaction progress of the DZ TCSCF TS ranges from -11 to 45%. The transition structure occurs at a value of reaction progress somewhat

(19) Furukawa, Y.; Takeuchi, H.; Harada, I.; Tatsumi, M. *Bull. Chem. Soc. Jpn.* **1983**, *56*, 392, and references cited therein.

Table IV. Geometries and Energies of the C_2 Transition Structures for the Conrotatory Electrocyclizations of Cyclobutene, *trans*-3,4-Dimethylcyclobutene, and *trans*-3,4-Dihydroxycyclobutene^a


	cyclobutene		3,4-dimethylcyclobutene		3,4-dihydroxycyclobutene	
	R _{in} = H; R _{out} = H 3-21G	R _{in} = H; R _{out} = H DZ TCSCF ^b	R _{in} = H; R _{out} = CH ₃ "outward"	R _{in} = CH ₃ ; R _{out} = H "inward"	R _{in} = H; R _{out} = OH "outward"	R _{in} = OH; R _{out} = H "inward"
Bond Lengths, Å						
C ₁ C ₄	1.421 (54)	1.462 (39)	1.422	1.416	1.420	1.422
C ₃ C ₄	2.138 (37)	2.238 (43)	2.147	2.209	2.110	2.200
C ₁ C ₂	1.369 (28)	1.351 (-11)	1.368	1.373	1.369	1.379
C ₃ R _{in}	1.071	1.079	1.072	1.529	1.068	1.408
C ₃ R _{out}	1.080	1.073	1.516	1.084	1.388	1.075
C ₁ H ₅	1.071	1.073	1.073	1.074	1.071	1.073
Bond Angles, deg						
C ₄ C ₁ C ₂	104.3 (29)	108.1 (41)	104.6	105.6	103.7	104.1
C ₄ C ₃ C ₂	73.4 (37)	70.8 (45)	73.3	71.8	74.0	71.5
R _{out} C ₃ R _{in}	114.3	115.1	114.8	111.4	109.5	106.5
R _{out} C ₃ C ₂	118.0	118.1	123.8	118.5	124.0	121.9
R _{in} C ₃ C ₂	122.5	122.1	116.4	122.2	119.1	123.4
H ₅ C ₁ C ₂	129.3	123.5	129.3	128.8	129.3	129.6
Dihedral Angles, deg						
C ₄ C ₁ C ₂ C ₃	21.9		21.5	24.4	22.0	31.2
C ₄ C ₃ C ₂ C ₁	14.5	16.4	14.2	15.6	14.8	20.0
H ₅ C ₁ C ₄ R _{out}	29.3	39.1	29.5	29.2	28.2	30.1
H ₅ C ₁ C ₄ R _{in}	123.8	115.3	124.2	118.4	118.6	114.0
H ₅ C ₁ C ₂ H ₆	31.5	17.1	32.0	37.1	31.4	38.3
R _{in} C ₄ C ₁ C ₂	60.8		60.9	67.7	65.9	69.4
R _{out} C ₄ C ₁ C ₂	146.5		145.4	144.7	147.3	146.5
BC ₄ C ₁ C ₂ ^c	42.9 (48)		42.3 (47)	38.5 (43)	40.7 (45)	38.6 (43)
Energies (au)						
3-21G//3-21G	-153.964 36		-231.611 15	-231.590 44	-302.85 827	-302.808 04
3-21G + ZPE	-153.873 79					
MP2/3-21G//3-21G	-154.332 72					
MP2/6-31G*/3-21G	-155.349 43					
Relative Energies (kcal/mol) ^d						
E ¹ (3-21G)	41.6	39.4	40.4	53.4	23.4	55.0
E _a (3-21G)	40.1					
E ¹ (MP2/3-21G)	32.8					
E _a (MP2/3-21G)	31.3					
E ¹ (MP2/6-31G*)	36.6					
ΔE _{rxn} (3-21G//3-21G)	-14.6	-5.0				
ΔE _{rxn} (exptl) ^e	-11.4					

^aNumbers in parentheses signify the reaction progress which is described in the text. ^bBreulet and Schaefer results, ref 5. ^cB is the bisector of the R_{out}CR_{in} angle. ^dE¹ is the difference between the energy of cyclobutene and the transition structure; E_a is the same quantity, corrected by zero-point energies of reactant and TS. ^eWiberg, K. B.; Fenoglio, R. A. *J. Am. Chem. Soc.* **1968**, *90*, 3395.

less than 50%, on the average, consistent with the slightly exothermic nature of the reaction.

The calculated 3-21G activation energy with zero-point energy corrections is 40.1 kcal/mol, 7.6 kcal/mol higher than the experimental activation energy, but only 0.7 kcal/mol higher than the DZ TCSCF activation energy. Inclusion of correlation energy corrections (MP2/3-21G//3-21G) lowers the activation energy to 32.8 kcal/mol (31.3 kcal/mol with zero-point energy corrections). For comparison, Schaefer obtained an activation energy of 35.8 kcal/mol by incorporating configuration interaction (DZ TCSCF + CISD). The exothermicity of the reaction is overestimated by 3.2 kcal/mol at the 3-21G RHF level, while Schaefer's DZ TCSCF calculations underestimate the exothermicity by 6.4 kcal/mol.

The 3-21G vibrational frequencies were calculated for both the reactant and the transition structure. In the transition structure, the imaginary vibrational frequency corresponds to the stretching of the C₃C₄ bond coupled with the conrotation of the two methylene termini. The magnitude of the 3-21G imaginary vibrational frequency is 262 cm⁻¹ larger than that of the Breulet-Schaefer TS. This difference is probably related to the 3-21G overestimate of the activation energy, which should lead to an overestimate of

the negative curvature of the potential surface along the reaction coordinate in the region of the TS.

***trans*-3,4-Dimethylcyclobutene.** The two 3-21G transition structures for *trans*-3,4-dimethylcyclobutene corresponding to the outward and inward rotations of the two methyl groups are shown in Figures 3 and 4, respectively. The geometries of these species are listed in Table IV.

The outward transition structure occurs slightly later than the cyclobutene TS. For example, the breaking C₃C₄ bond length in the outward TS is 0.01 Å longer than the corresponding bond length in the parent TS, while the C₁C₄ and C₁C₂ bond lengths are virtually identical for both structures. The bond angles (excluding angles involving the methyl groups) and dihedral angles differ at most by 1°.

The inward TS is more advanced than the outward TS. The breaking C₃C₄ bond length in the inward TS is 0.06 Å longer than that of the outward, while the C₁C₂ and C₁C₄ bond lengths are slightly longer and shorter, respectively, in the inward TS. The differences in dihedral angles further reflect the more advanced nature of the inward TS. For example, the C₄C₁C₂C₃ and H₅C₁C₂H₆ dihedral angles of the inward TS are 3 and 5° larger than the corresponding dihedral angles of the outward TS.

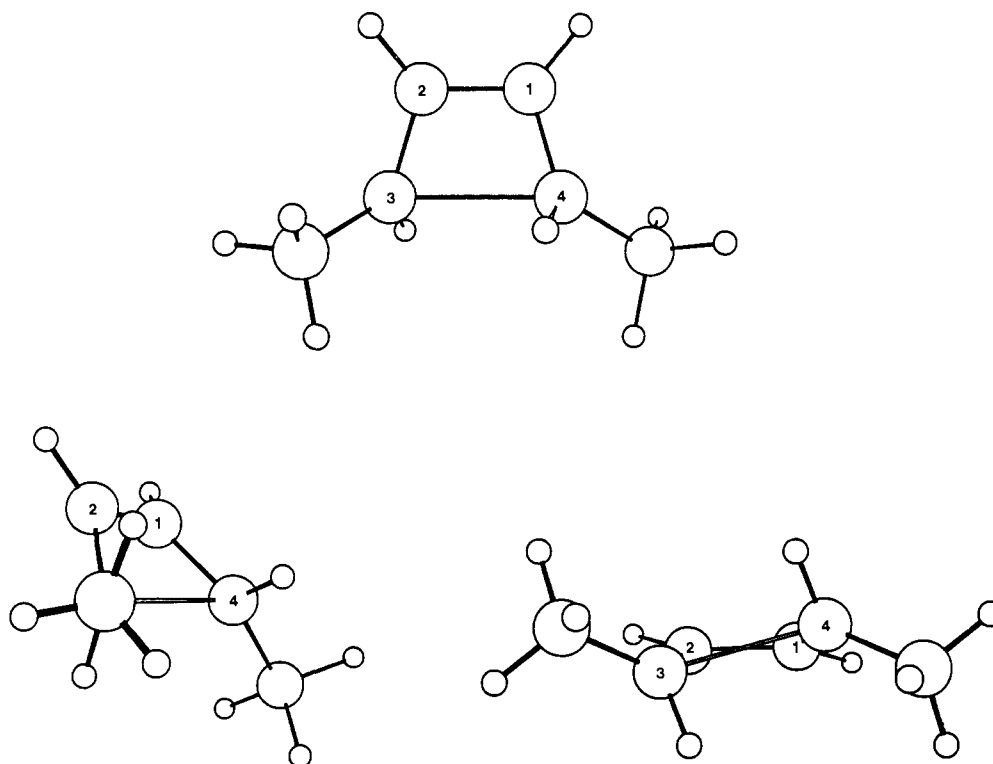


Figure 3. Three views of the "outward" 3-21G transition structure for the conrotatory electrocyclic reaction of *trans*-3,4-dimethylcyclobutene.

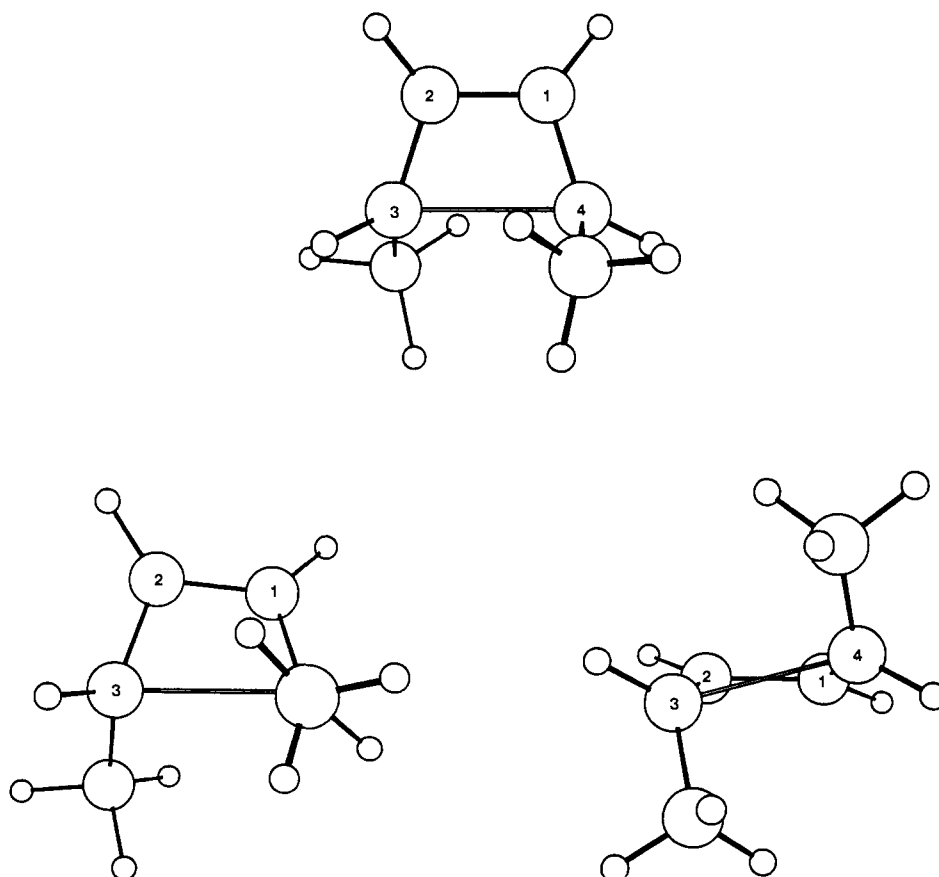


Figure 4. Three views of the "inward" 3-21G transition structure for the conrotatory electrocyclic reaction of *trans*-3,4-dimethylcyclobutene.

However, the degrees of rotation of the CHCH_3 termini are less for the inward TS. The dihedral angle $\text{BC}_4\text{C}_1\text{C}_2$, which measures the CHCH_3 termini rotation, is 38.5 and 42.3° for the inward and the outward TS, respectively. The repulsive interactions of methyls upon inward rotation, due both to steric and electronic effects (see below), are undoubtedly responsible for the relative

lateness of the inward TS. That is, rotation is resisted and an increase in the angle $\text{C}_4\text{C}_1\text{C}_2\text{C}_3$ occurs until the bond lengths and angles are reorganized toward the diene product structure.

The CC bond lengths of the methyl groups that rotate inward are longer than those of the outward rotating methyl groups, indicative of repulsive interactions for the former. In both

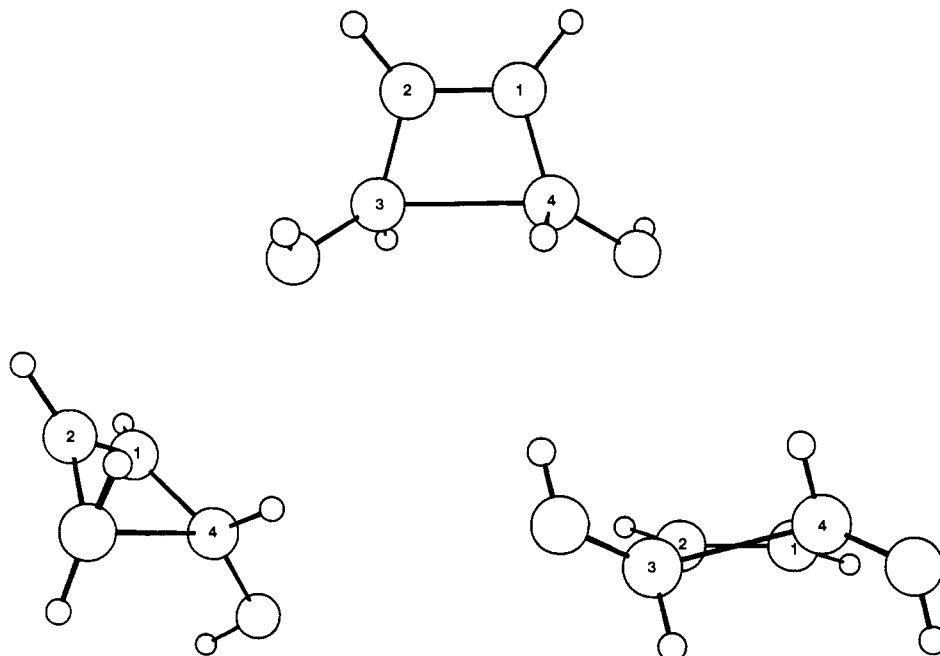


Figure 5. Three views of the "outward" 3-21G transition structure for the conrotatory electrocyclic reaction of *trans*-3,4-dihydroxycyclobutene.

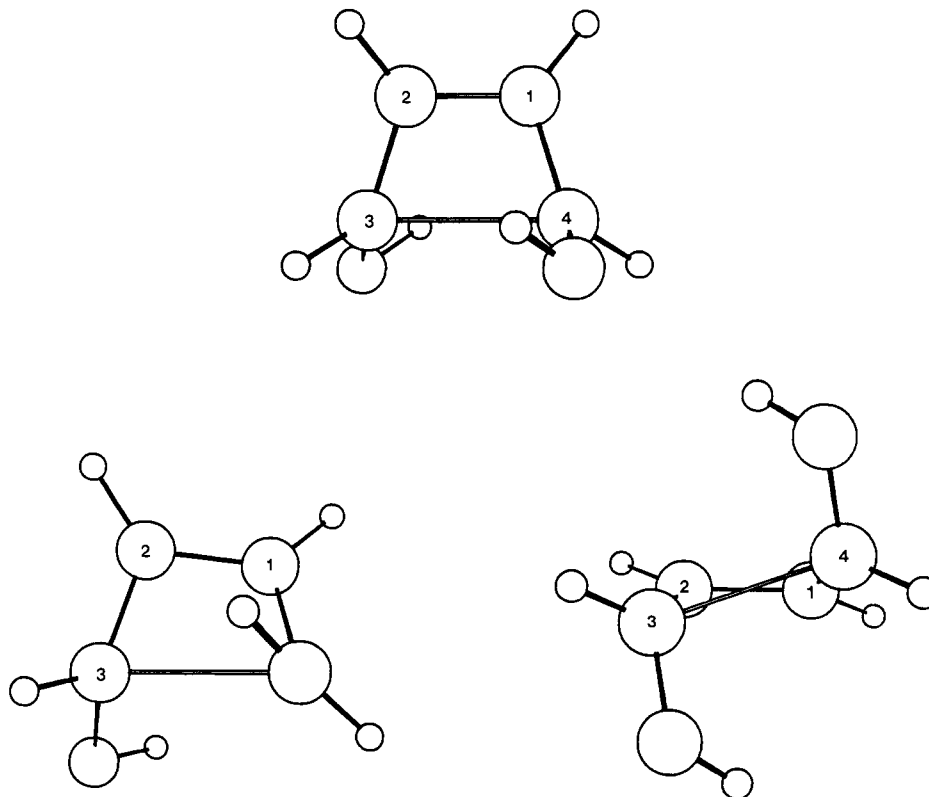


Figure 6. Three views of the "inward" 3-21G transition structure for the conrotatory electrocyclic reaction of *trans*-3,4-dihydroxycyclobutene.

transition structures the methyl hydrogens are staggered with respect to the bonds to C₃ and C₄.

The 3-21G activation energy for the outward *trans*-3,4-dimethylcyclobutene reaction is 1.2 kcal/mol lower than that of the cyclobutene reaction, in reasonable agreement with the 1.9 kcal/mol difference found experimentally. The outward dimethylcyclobutene TS leading to the *E,E* isomer is 13.0 kcal/mol more stable than the inward TS. From methyl additivities (Table II), this difference is expected to be 8 kcal/mol in favor of the outward rotations of the two methyl groups. The calculations overestimate this difference by about 60%.

***trans*-3,4-Dihydroxycyclobutene.** Hydroxy groups were chosen as model donor substituents and to model the electronically similar,

but larger (and more expensive to calculate) alkoxy groups. The outward and inward transition structures for the conrotatory electrocyclic reactions of *trans*-3,4-dihydroxycyclobutene are depicted in three different views in Figures 5 and 6, respectively. In both transition structures, the OH bonds are pointed inside the cyclobutene ring and are staggered with respect to the bonds to C₃ and C₄ (see Newman projection about CO bond in the lower left of Figures 5 and 6). Other conformations were investigated by rigid rotation around the CO bond starting from the fully optimized inward or outward transition structures. These conformations were all less stable than those shown in Figures 5 and 6.

The outward TS again occurs earlier than the inward, as shown

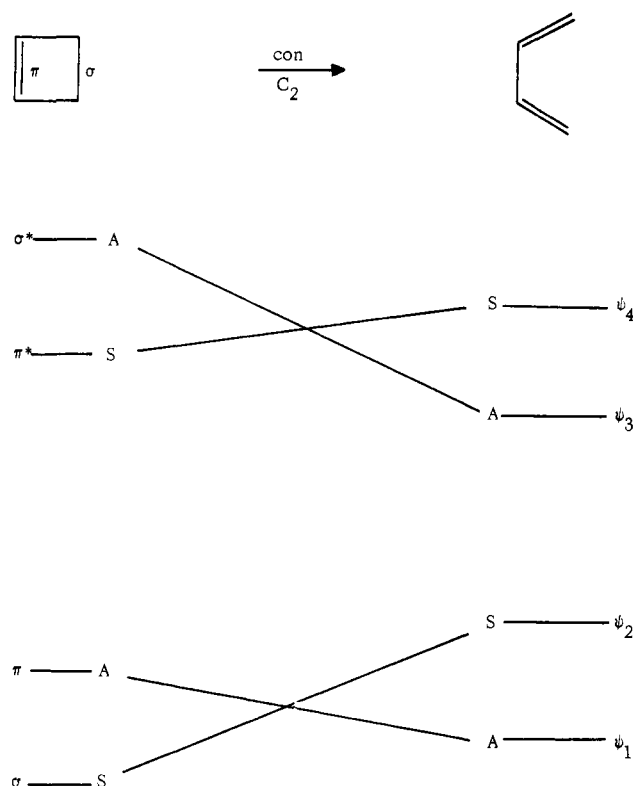


Figure 7. Woodward-Hoffmann correlation diagram for the conrotatory electrocyclization of cyclobutene.

by the longer C_3C_4 bond length for the latter TS, and the differences in the dihedral angles involving the four cyclobutene carbons. The $C_4C_1C_2C_3$ and $C_4C_3C_2C_1$ dihedral angles in the outward TS are 9 and 5° smaller than those of the inward TS. The inward CO bond length (1.408 Å) is longer than the outward CO bond length (1.388 Å). This is a consequence of the greater destabilizing interaction in the inward TS between the oxygens and the cyclobutene skeletal atoms (see later).

The 3-21G activation energy for the outward TS is 23.4 kcal/mol, 18.2 kcal/mol lower than that for cyclobutene. As noted earlier, assuming additivity of substituent effects at C_3 and C_4 , alkoxy groups which rotate outward lower the activation energy by 9 kcal/mol each, for a total lowering of 18 kcal/mol for *trans*-3,4-alkoxycyclobutene. Here there is perfect agreement of calculations with experiment.

The inward TS, on the other hand, is 31.6 kcal/mol higher in energy than the outward TS, similar to the experimentally estimated difference of 28 kcal/mol (Table II).

Origin of Stereoselective Substituent Effects on Electrocyclizations

The large difference in activation energies between the outward and inward rotations of the hydroxy groups in *trans*-3,4-dihydroxycyclobutene is too large to be attributed solely to steric effects. The pyramidalizations of the olefinic carbons in the reactants, noted by Dolbier,¹⁰ are too small to be the determinants of the stereochemistries of the reactions. The out-of-plane angles of the vinylic hydrogens are only 0.5 and 0.6° for *trans*-3,4-dihydroxycyclobutene and *trans*-3,4-dimethylcyclobutene, respectively (Table III).

We have devised a new theoretical model to explain the stereochemistries of the electrocyclizations of cyclobutenes. In order to understand the model, it is necessary to recall the Woodward-Hoffmann correlation diagram for a conrotatory electrocyclization. This is shown in Figure 7. The correlation lines, which connect orbitals of the same symmetry, show that the reactant orbitals smoothly correlate with those of the product, the hallmark of a thermally allowed reaction.² However, even thermally allowed reactions have substantial barriers, since the reactant resists the evolution of its electronic structure into that

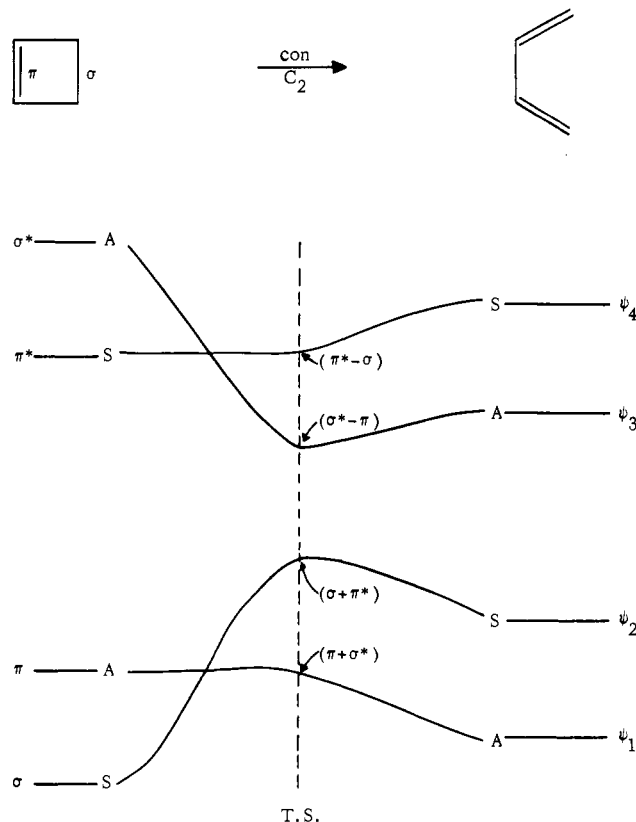


Figure 8. Schematic representation of the behavior of the orbitals involved in bonding changes in the conrotatory electrocyclization of cyclobutene.

of the product until substantial geometrical distortions occur. Thus, the behavior of the orbitals along the reaction pathway is not the linear change implied by Figure 7, but is reflected more accurately instead by Figure 8.

As described for the cyclobutene electrocyclic reaction by Woodward and Hoffmann,² and by Houk et al. for pericyclic reactions in general,²⁰ the behavior of the frontier molecular orbitals during an allowed pericyclic reaction reflects the "intended correlation" of the orbitals involved in the breaking and forming bonds. Similar ideas have been noted by Devaquet et al. for photochemical reactions,²¹ and by Jorgensen for the Diels-Alder reaction.²² The stretching of the C_3C_4 σ bond of cyclobutene is accompanied by a rapid increase in energy. If conrotation occurred without mixing of this stretched σ orbital with other orbitals, an orbital which resembled (in symmetry properties) the LUMO of butadiene would be formed. At the same time, σ^* would correlate with the HOMO of butadiene. Indeed, the initial rapid destabilization of σ and stabilization of σ^* in Figure 8 is a reflection of this tendency.

However, when σ is destabilized sufficiently to be close in energy to π^* , and when rotation of the termini allows mixing of σ with π^* , then rapid stabilization occurs. Similarly, at some point along the reaction coordinate, the mixing of σ^* with π begins, leading to a destabilization of the orbital derived from σ^* . The transition structure of a reaction is near the point where the stabilization resulting from $\sigma-\pi^*$ and $\sigma^*-\pi$ mixing becomes substantial enough to overcome the energy required to distort the molecules. At this point, reaction progress carries the molecule into a geometry which is essentially that of a distorted product.

At the transition structure, the HOMO is essentially the stretched $\sigma_{C_3C_4}$ orbital of the distorted cyclobutene, mixed to a

(20) Houk, K. N.; Gandour, R. W.; Strozier, R. W.; Rondan, N. G.; Paquette, L. A. *J. Am. Chem. Soc.* **1979**, *101*, 6797.

(21) Devaquet, A.; Sevin, A.; Bigot, B. *J. Am. Chem. Soc.* **1978**, *100*, 2009.

(22) Jorgensen, W. L. Cited in: Townshend, R. E.; Ramuni, G.; Segal, G.; Hehre, W. J.; Salem, L. *J. Am. Chem. Soc.* **1976**, *98*, 2190.

Table V. 3-21G Relative Energies and FMO Energies of Model Transition Structures in Electrocyclic Reactions of Substituted Cyclobutenes^a

	E_{rel} (kcal/mol)	E_{HOMO} (eV)	E_{LUMO} (eV)
<i>trans</i> -3,4-dimethylcyclobutene			
outward	0.0 (0.0)	-8.26 (-8.19)	4.27 (4.21)
inward	+20.9 (+13.0)	-7.79 (-7.93)	3.75 (3.71)
<i>trans</i> -3,4-dihydroxycyclobutene ^b			
outward	0.0(0.0)	-8.20 (-8.11)	4.31 (4.25)
inward	+45.9 (+31.6)	-7.26 (-7.71)	3.11 (3.52)
3-fluorocyclobutene			
outward	0.0	-9.07	3.86
inward	+20.8 [13]	-8.48	3.38
<i>trans</i> -3,4-difluorocyclobutene			
outward	0.0	-9.21	3.81
inward	+40.7 [29]	-8.18	2.88
<i>trans</i> -3,4-dichlorocyclobutene			
outward	0.0	-9.93	2.14
inward	+31.3 [22]	-8.93	2.07
<i>trans</i> -3,4-diaminocyclobutene ^c			
outward, NH ₂ lone-pair parallel to C ₃ C ₄	0.0	-6.47	5.23
inward, NH ₂ lone-pair parallel to C ₃ C ₄	+51.7 [36]	-5.66	3.99
outward, NH ₂ lone-pair perpendicular to C ₃ C ₄	+16.9	-8.61	4.17
inward, NH ₂ lone-pair perpendicular to C ₃ C ₄	+50.0 [35]	-7.11	3.51
<i>trans</i> -3,4-dicyanocyclobutene			
outward	0.0	-10.12	0.65
inward	+12.4 [9]	-9.67	1.10
<i>trans</i> -3,4-diborylcyclobutene ^d			
outward, BH ₂ p orbital parallel to C ₃ C ₄	+17.8 [13]	-9.47	0.49
inward, BH ₂ p orbital parallel to C ₃ C ₄	0.0	-9.80	2.34

^aNumbers in parentheses are the values obtained from the fully optimized transition structures. Numbers in brackets are rough predictions of the experimental differences in energy for "outward" and "inward" rotations, assuming that estimated differences from model transition structures are 70% too large. ^bThe OH conformation is staggered, with the OH bond directed inside the cyclobutene ring. ^cThe amino group was fixed planar. ^dThe boryl group was fixed planar.

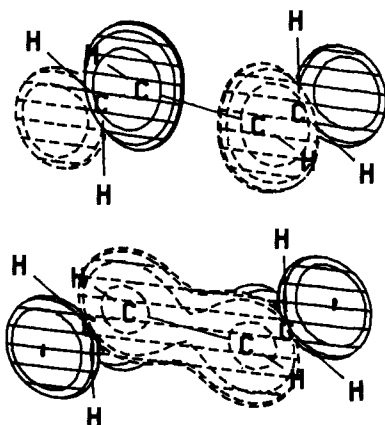


Figure 9. STO-3G HOMO ($\sigma + \pi^*$) and LUMO ($\sigma^* - \pi$) of the 3-21G cyclobutene transition structure.

small extent with π^* . The LUMO is primarily σ^* , mixed in an antibonding fashion with π .

These frontier MO's, drawn with Jorgensen's orbital plotting program²³ with the STO-3G basis set on the 3-21G TS geometry, are shown in Figure 9. The highest occupied molecular orbital (HOMO) is essentially the σ orbital of the breaking C₃C₄ bond, mixed in bonding fashion with the C₁C₂ π^* orbital ($\sigma + \pi^*$). This is the orbital that evolves into the HOMO of butadiene in the product.² The lowest unoccupied molecular orbital (LUMO) is mainly the σ^* orbital of C₃C₄ mixed in negative fashion with the C₁C₂ π orbital. This orbital correlates with the LUMO of the butadiene product.² The second highest molecular orbital (SHOMO) is the C₁C₂ π orbital mixed in a bonding fashion with the σ^* orbital of C₃C₄, while the second lowest unoccupied orbital

(SLUMO) is the antibonding combination between the C₃C₄ σ orbital and the C₁C₂ π^* orbital. These orbitals become the lowest π and highest π^* orbitals of the product.

trans-3,4-Dimethyl substitution perturbs the HOMO and LUMO of the outward and inward TS to different extents. The outward HOMO is 0.26 eV lower in energy than the inward HOMO, while the outward LUMO is 0.50 eV higher than the inward LUMO (see Table V). This suggests that the preferential formation of (*E,E*)-hexadiene over the (*Z,Z*) isomer is due not only to steric effects, but also to electronic effects, as manifested by the larger HOMO-LUMO gap for the outward transition structure than for the inward. The origin of this electronic difference is described in more detail below.

The frontier molecular orbitals of the outward and inward transition structures of *trans*-3,4-dihydroxycyclobutene are shown in Figure 10. The HOMO in both transition structures is the C₃C₄ σ orbital, mixed in a bonding fashion with the C₁C₂ π^* orbital and also in an antibonding fashion with the positive combination of the oxygen lone-pair orbitals ($\sigma + \pi^* - n_+$). The outward HOMO is lower in energy (-8.11 eV) than the inward HOMO (-7.71 eV). Although both HOMO's are destabilized by the antibonding interactions between the C₃C₄ σ and the oxygen lone-pair orbitals, there is greater destabilization in the inward TS because of the proximity of the lone pairs to the remote terminus of the C₃C₄ σ orbital. The greater overlap of the n_+ lone-pair orbital with the C₃C₄ σ orbital upon inward rotation results in greater closed-shell, or four-electron, repulsion, since both of these orbitals are doubly occupied. The same pattern would occur in a 3-monoalkoxycyclobutene, where oxygen lone-pair overlap would be greater for inward rotation than for outward rotation, leading to greater repulsion in the former case.

The LUMO of both the outward and the inward transition structures is largely the C₃C₄ σ^* mixed in antibonding fashion with both the C₁C₂ π and the negative combination of the oxygen lone-pair orbitals ($\sigma^* - \pi - n_-$). The outward LUMO is 0.73 eV higher in energy than the inward LUMO. The energy of the LUMO indirectly signals the extent of the stabilizing interaction

(23) We thank Professor W. L. Jorgensen and Mr. David C. Spellmeyer for the Harris version of the orbital plotting program.

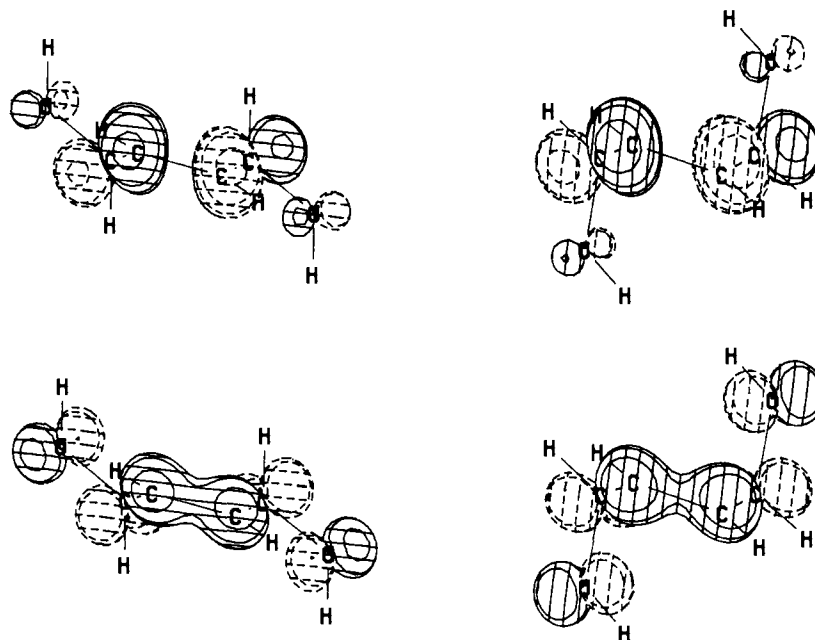


Figure 10. STO-3G frontier molecular orbitals for the 3-21G "outward" and "inward" *trans*-3,4-dihydroxycyclobutene transition structures.

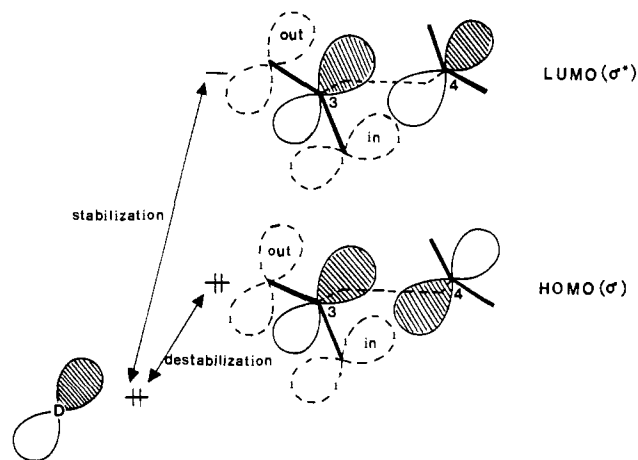


Figure 11. Schematic representation of donor orbital interactions with the HOMO and LUMO of the cyclobutene conrotatory electrocyclic transition structure. The dashed lines represent the position of the donor orbital upon "outward" (labeled out) or "inward" (labeled in) rotation.

between a donor lone-pair orbital and the low-lying vacant C_3C_4 σ^* orbital. This interaction is a stabilizing two-electron interaction, and the extent of stabilization increases as the extent of overlap between these orbitals increases. The higher energy of the outward LUMO arises because the overlap of donor orbitals with σ^* is larger, which results in more stabilization of the occupied donor orbitals, and thus of the transition structure overall. Overlap of the oxygen lone-pair orbitals with the distorted σ^* orbital is greater upon outward rotation than upon inward. Upon outward rotation, there is overlap of the donor p orbital primarily with the orbitals on the attached carbon atom. Upon inward rotation, the donor orbital overlaps with atomic orbitals on the attached carbon, and on the remote carbon. Since these have opposite signs, the net overlap is less upon inward rotation.

Figure 11 is a sketch of the transition structure HOMO and LUMO, with the placement of the donor orbital sketched in for either outward (out) or inward (in) rotation. Upon outward rotation, the donor orbital appreciably overlaps only with the hybrid orbital on the attached atom. As noted earlier, a donor substituent lowers the activation energy for ring opening upon outward rotation. This is due to the substantial stabilization which arises from the interaction of the donor orbital with the σ^* transition structure LUMO. At the same time, there is a smaller repulsion arising from donor orbital interaction with the σ HOMO

of the transition structure. Upon inward rotation of the donor, the stabilizing interaction of the donor orbital with σ^* is much less due to diminished overlap of these two. Here the donor orbital points toward a nodal surface of the σ^* and overlap is small. The repulsive interaction of donor with σ now dominates, owing to the increased overlap of these orbitals. This repulsion dominates, and donor substituents increase the activation energy for inward rotation.

These differences in interactions are shown in more detail by the shapes and energies of the molecular orbitals of the transition structures. Figure 12 shows the orbital interactions in detail for a single donor orbital (on OH, for example). The interaction of a high-lying donor orbital of the substituent (π_{CH_3} on CH_3 or lone pair on a heteroatom) with the $\sigma^*_{C_3C_4}$ orbital is a stabilizing two-electron interaction. The overlap between these orbitals is larger for outward rotation than for inward. Upon outward rotation, the donor orbital mixes with σ^* and σ . The former, two-electron interaction dominates, and the transition structure is stabilized. Upon inward rotation, overlap of the donor orbital with σ^* is less, because of the vicinity of the donor orbital to the orbital on the remote terminus of the sketched σ^* orbital. As a result, the occupied donor orbital is stabilized less, and the vacant σ^* is destabilized less. Figure 12 shows this schematically, and the shapes of the LUMOs in Figure 10 and LUMO energies described earlier confirm this interaction. Thus, there is considerably less stabilization upon inward donor rotation than upon outward donor rotation. Some of the transition structure stabilization is counteracted by destabilizing four-electron interaction between the donor orbital on the substituent and the $\sigma_{C_3C_4}$ orbital. Both of these orbitals are occupied, so the greater the overlap, the greater the repulsive four-electron interaction. Since the overlap is larger for inward rotation, repulsion is larger. This is reflected in the higher HOMO energies of transition structures for inward rotation. Indeed, repulsion dominates the inward rotation. This is a specific electronic effect which depends upon the donor character, rather than the size, of the substituent. To describe this effect in its simplest form, inward rotation of a donor is disfavored because this results in a cyclic array of orbitals occupied by four electrons (or a Möbius six-electron array if the π bond is included in the electron count). Outward rotation results in a linear acyclic array of orbitals with four electrons. Outward rotation leads to a nonaromatic interaction, while inward rotation produces destabilizing antiaromatic interaction.

The orbital correlation diagram given in Figure 8 also facilitates understanding of the influence of substituents on the activation energies for ring opening. A substituent which decreases the $\sigma-\pi^*$

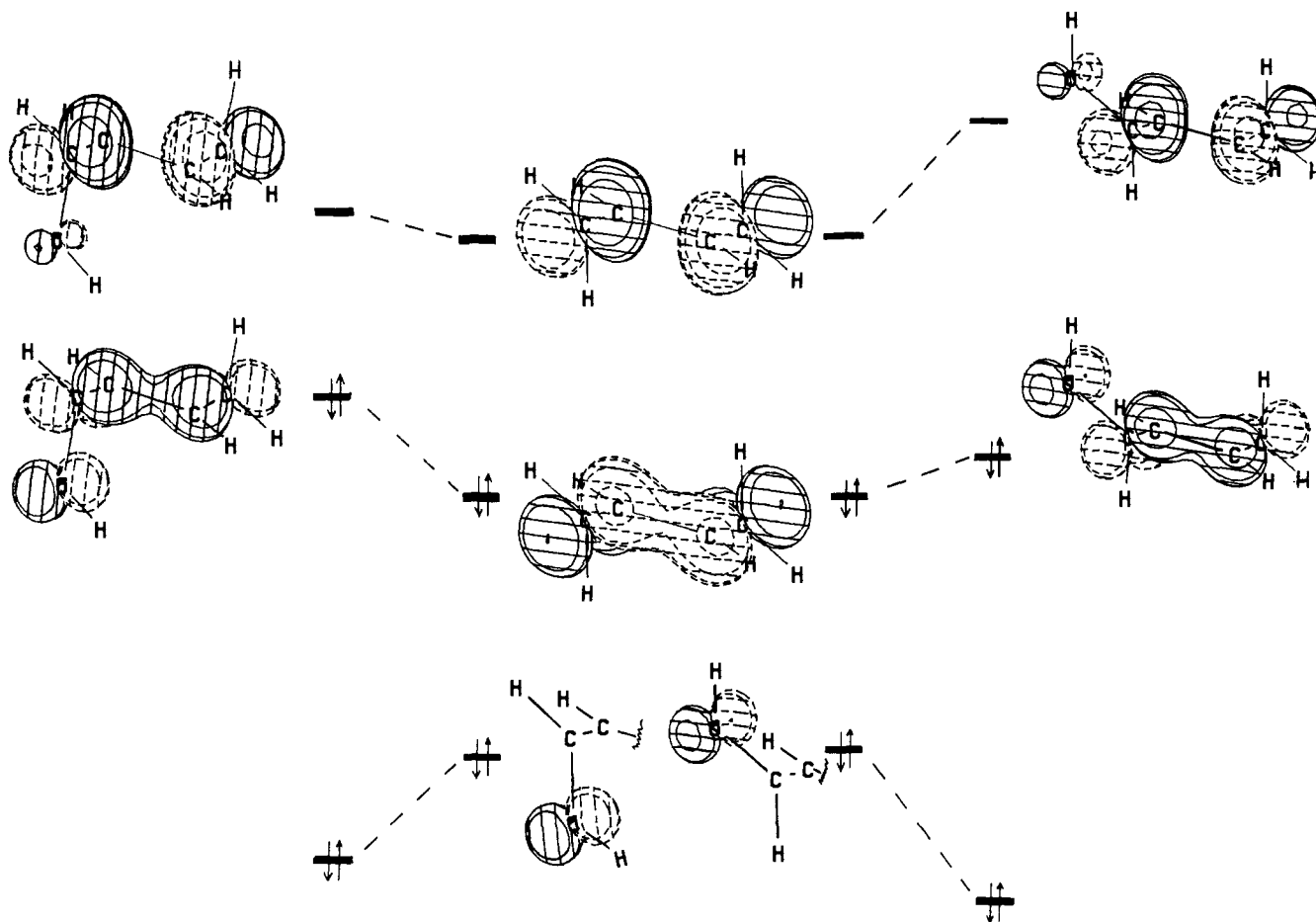


Figure 12. Orbital interactions which influence the stereoselectivity of the conrotatory electrocyclic reactions of substituted cyclobutenes.

or π - σ^* gap will cause the transition structure to occur earlier, since mixing of these orbitals can occur with less breaking of the σ bond required. Thus, a donor or acceptor at any position should help, since donors can raise either σ or π orbitals and acceptors lower either σ^* or π^* orbitals. The best combination should be donors at both C-3 and C-4 and acceptors at both C-1 and C-2, or vice versa.

Model Calculations for Other Substituents

Several model calculations were carried out to test the validity of this explanation. Single-point 3-21G calculations were carried out on other *trans*-3,4-disubstituted cyclobutene model transition structures which were constructed from the parent cyclobutene TS and standard substituent parameters. The results of these model calculations are summarized in Table V.

Model calculations on *trans*-3,4-dimethylcyclobutene overestimate the difference in energy of the outward and inward transition structures by 8.0 kcal/mol when compared with the energy difference in the fully optimized transition structures. Nevertheless, the orbital energy trends are identical. That is, in both calculations, the outward HOMO-LUMO gaps are larger than the inward HOMO-LUMO gaps. The model transition structures are expected to overestimate energy differences between inward and outward transition structures, since optimizations would decrease the unfavorable interactions most for the less stable transition structure. For the two cases tested, the model transition structure calculations overestimate the energy difference by 60-70%.

Model calculations on the heterosubstituted cyclobutenes revealed several interesting results. Although all heterosubstituents prefer to rotate outward, the energy differences between the outward and inward transition structures increase along the series $\text{Cl} < \text{F} < \text{OH} < \text{NH}_2$. This trend parallels increasing electron donation by the substituents. Ionization potentials (IPs) can be used to assess the electron-donating ability of the substituents.

As the ionization potential decreases, the electron-donating ability of the substituent increases. The lone-pair ionization potentials of HNH_2 , HOH , and HF are 10.18,²⁴ 12.60,²⁵ and 16.03 eV,²⁶ respectively. Chlorine does not fit into the IP vs. donor relationship because ionization occurs from a 3p orbital. Although the IP of HCl is lower (12.72)²⁷ than that of HF , the overlap of the Cl 3p orbitals with C 2p orbitals is smaller than that of fluorine 2p orbitals. Thus, there is a smaller interaction of Cl lone pairs with the C_3C_4 σ and σ^* orbitals. The σ^*_R values can also be used to evaluate the electron-donating ability of these substituents. The σ^*_R values of Cl, F, OCH_3 , and NH_2 are -0.36, -0.57, -1.02, and -1.61, respectively,²⁸ which reflect both IP and overlap effects. These values parallel the influence of substituents upon activation energies, and the difference in activation energies for inward and outward rotation. In general, the better the donor, the greater the preference of the outward transition structure.

The effect of substituents at C₃ and C₄ on the energy difference between the two transition structures is predicted to be very nearly additive. For example, while the outward transition structure for 3-fluorocyclobutene is preferred over the inward by 20.8 kcal/mol, the energy difference increases to 40.7 kcal/mol in going to *trans*-3,4-difluorocyclobutene (cf. entries 3 and 4). Thus, the direct interaction between substituents is unlikely to have any effect upon the activation energies for these reactions.

Calculations on the amino cases were carried out on planar amino groups in two different conformations. For the outward

(24) Aue, D. H.; Webb, H. M.; Bowers, M. T. *J. Am. Chem. Soc.* **1975**, *97*, 4136.

(25) Debies, T. P.; Rabalais, J. W. *J. Am. Chem. Soc.* **1975**, *97*, 487.

(26) Berkowitz, J. *Chem. Phys. Lett.* **1971**, *11*, 21.

(27) Tiedemann, P. W.; Anderson, S. L.; Ceyer, S. T.; Hirooka, T.; Ng, C. Y.; Mahan, B. H.; Lee, Y. T. *J. Chem. Phys.* **1979**, *71*, 605.

(28) Ehrenson, S.; Brownlee, T. C.; Taft, R. W. *Prog. Phys. Org. Chem.* **1973**, *10*, 1.

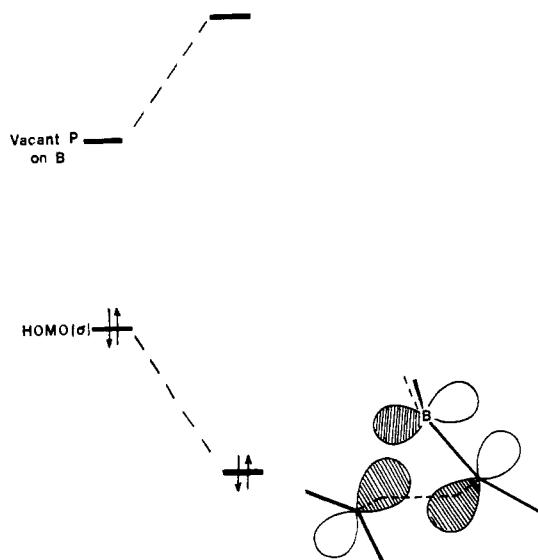


Figure 13. Orbital interactions between the borane vacant p orbital and the $\sigma_{C_3C_4}$ in the transition structure of the electrocyclic reactions. Dashed lines represent the position of the vacant p orbital upon "outward" and "inward" rotation.

rotation of both amino groups, the model transition structure with the amino lone-pair donor orbitals aligned parallel to the breaking C_3C_4 σ bond is 17 kcal/mol more stable than that with the amino groups rotated by 90° , which eliminates the amino lone-pair overlap with $\sigma_{C_3C_4}$ and $\sigma^*_{C_3C_4}$.

If the lone pairs are aligned with the C_3C_4 bond, the outward rotation by the NH_2 group is preferred by 51.7 kcal/mol, whereas the preference decreases to 33.0 kcal/mol upon removal of NH_2 lone-pair interaction with the σ and σ^* orbitals at C_3C_4 . This is consistent with the idea that the N lone-pair C_3C_4 interaction is important in lowering the activation energy for outward rotation, but steric effects must also contribute to the destabilization of the inward transition structures. The transition structures in Figures 5 and 6 also show that the donor orbitals of the hydroxys align almost perfectly with σ^* in the preferred outward transition structures, but the donor orbital is rotated somewhat to relieve overlap with σ in the disfavored inward transition structure.

trans-3,4-Dicyanocyclobutene might be expected to prefer the inward transition structure because of the low-lying vacant orbitals of the cyano group. That is, one would expect that the stabilizing two-electron interaction of the cyano π^* orbitals with the C_3C_4 σ orbital would be greater for the inward transition structure than for the outward. However, calculations indicate that the outward transition structure is still preferred by 12.4 kcal/mol, suggesting that the interaction of the filled π orbitals of the cyano group²⁹ with σ overpowers the effect of vacant orbitals.

An extreme acceptor substituted cyclobutene was modeled by using the BH_2 group with the empty p orbital on boron aligned parallel to the $\sigma_{C_3C_4}$ orbital. For *trans*-3,4-diborylcyclobutene, the inward transition structure is preferred over the outward by 17.8 kcal/mol. The inward preference is observed because the two-electron interaction between the C_3C_4 σ orbital and the empty p orbitals of the boryl groups is greater for the inward transition structure than for the outward. The inward HOMO and LUMO are now more stable than the outward HOMO and LUMO (see entry 8). These interactions are summarized in Figure 13.

Summary and Predictions

The stereochemistries of the thermal electrocyclic conrotatory opening of *trans*-3,4-disubstituted cyclobutene can be rationalized

on the basis of electronic effects. We have demonstrated computationally that electron donors at C_3 and C_4 preferentially rotate outward in order to maximize the stabilizing two-electron interaction between the donor orbitals on the substituent with the $\sigma^*_{C_3C_4}$ orbital and to minimize the repulsive four-electron interaction between the same donor orbitals with the $\sigma_{C_3C_4}$ orbital. We have also shown that the preference for outward rotations of the substituents increases as the electron-donor ability of the substituents increases. Powerful electron acceptors should have the opposite effect, and, consequently, opposite stereochemical results are predicted.

For 3,3-disubstituted and *cis*-3,4-disubstituted cyclobutenes, our model would predict that the stronger electron donor would preferentially rotate outward, while the weaker donor rotates inward. For example, we would predict that 3-chloro-3-fluorocyclobutene would give (*Z*)-1-chloro-1-fluorobutadiene, opposite to what one would expect if steric effects are involved. Similar predictions can be made for other 3,3-disubstituted cyclobutenes, and experimental results concur.⁹ For *cis*-3,4-disubstituted cyclobutenes, many experimental results are in accord with this expectation. For example, *cis*-3-chloro-4-methoxycyclobutene affords (*Z*)-1-chloro-(*E*)-4-methoxybutadiene (Table I).

Dolbier's experimental results¹⁰ can be rationalized on the basis of electronic effects. F is a considerably better donor than CF_3 . Thus, fluorine preferentially rotates outward, while CF_3 rotates inward, in spite of steric effects in the opposite direction. Since we predict a 30-kcal/mol preference for two fluorines to rotate outward, there must be a counteracting 12-kcal/mol steric effect which prefers outward CF_3 rotation. The *trans*-difluorocyclobutene should exhibit an even larger preference for outward fluorine rotation. When fluorine is forced to rotate inward, activation energies should be quite high. Thus, 3,3,4,4-tetrafluorocyclobutene has a 16-kcal/mol higher activation energy than is observed for the cyclobutene.³⁰

Powerful π -electron acceptors are likely to show little stereochemical preference, since the acceptor character favors inward rotation, while the inevitably present filled orbitals on most substituents should promote outward rotation. Indeed, experimental results on species with ester or keto substituents at C_3 or C_4 indicate little or no preference for inward or outward rotation.¹

The reasonable agreement between the RHF 3-21G transition structure and that obtained at the DZ TCSCF level, the good activation energy estimate obtained with MP2/3-21G//3-21G calculations, and the relatively accurate calculation of substituent effects obtained even at the 3-21G level suggest that the 3-21G level with MP2/3-21G energies should be an acceptable level for the general investigation of pericyclic reactions, and substituent effects on these reactions. Borden et al. have found that RHF and MCSCF calculations give similar geometries for the transition structures of the Cope rearrangement, but neglect of correlation energy causes the RHF activation energy to be ≈ 10 kcal/mol too high,³¹ while we have found that the RHF 3-21G activation energies for 1,5-sigmatropic hydrogen shifts are similarly 6–10 kcal/mol too high, but can be corrected by MP2/3-21G//3-21G calculations.³² Thus, general investigations and solutions to the vexing problem of pericyclic reaction substituent effects^{14,15} should be possible at this level of theory.

Finally, the stereoselective substituent effects elucidated here should also operate to some extent in other electrocyclic and pericyclic processes. In common 6π electrocyclic reactions,^{1,2} the strongest donor substituent should rotate outward, to maximize two-electron stabilization and to minimize four-electron destabilization, while acceptors should show only low stereoselectivity, or prefer inward rotation in extreme cases. However, the effects for the 6π systems should be smaller than for cyclobutenes, since the orbital at the terminus of the breaking σ bond remote from the substituent does not point directly toward the substituent

(29) Experiment and theory have shown that cyano groups are capable of π donation, along with the usual π withdrawal. (a) Gassman, P. G.; Talley, J. J. *J. Am. Chem. Soc.* **1980**, *102*, 1214. (b) Paddon-Row, M. N.; Santiago, C.; Houk, K. N. *Ibid.* **1980**, *102*, 6561. Dixon, D. A.; Charlier, P. A.; Gassman, P. G. *Ibid.* **1980**, *1202*, 3597.

(30) Frey, H. M.; Hopkins, R. G.; Vinall, I. C. *J. Chem. Soc., Faraday Trans. 1* **1972**, *68*, 1874.

(31) Osamura, Y.; Kato, S.; Morokuma, K.; Feller, D.; Davidson, E. R.; Borden, W. T. *J. Am. Chem. Soc.* **1984**, *106*, 3362.

(32) Rondan, N. G.; Houk, K. N. *Tetrahedron Lett.* **1984**, 2519.

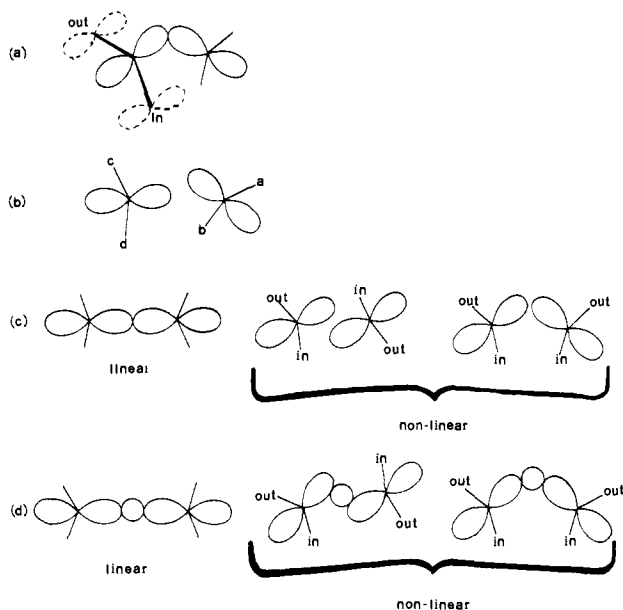


Figure 14. Expected shapes of FMOs of (a) 1,3-cyclohexadiene in the transition structure for the disrotatory electrocyclic reaction, (b) the FMOs of cyclopropane in a monorotatory isomerization, (c) linear and nonlinear CC bond-breaking processes, and (d) linear and nonlinear hydrogen shifts.

orbital (see Figure 14). The stronger the donor, the greater the tendency for outward rotation, while acceptors should show a smaller preference. Cyclopropane isomerizations involve the breaking of σ bonds and mainly the rotation of only one terminus.³³

As shown in Figure 14b, donors should prefer location a at the rotating terminus and c at the stationary terminus, while strong acceptors may prefer site b at the rotating terminus and d at the nonrotating. In general, for reactions which involve σ bond breaking in a linear fashion (Figure 14c), no stereochemical preference of the type described above is possible, but for nonlinear processes, donors will prefer the site which minimizes overlap with the breaking bond, while acceptors will seek to maximize such overlap. Similarly, in sigmatropic shifts, stereoselectivity may be influenced by overlap of substituents with the bonds to the migrating atom. As demonstrated in Figure 14d, no effect is possible for a linear hydrogen transfer, but for nonlinear transfer the effects are qualitatively similar to those described for electrocyclicization. Donor substituents will prefer to be located on the positions marked "out", while very strong acceptors may prefer to move "in".

The ramifications of these effects are being investigated in these laboratories.

Acknowledgment. We are grateful to the National Science Foundation for financial support of this research, to Professors Wolfgang Kirmse and William R. Dolbier, whose experimental results and suggestions prompted this study, and to the Alexander von Humboldt Foundation for a U.S. Senior Scientist Award to K.N.H., which made the collaboration with Professor Kirmse possible.

Registry No. Cyclobutene, 822-35-5; *trans*-3,4-dimethylcyclobutene, 1517-13-1; *trans*-3,4-dihydroxycyclobutene, 95070-00-1.

(33) Baldwin, J. E.; Barden, T. C., *J. Am. Chem. Soc.* **1984**, *106*, 5312, and references therein.

Mechanisms for Interconversions among C_3H_4 Hydrocarbons: Deuterium Isotope Effects and Independent Generation of Vinylmethylene Intermediates in Photoisomerizations of Allenes and Cyclopropenes

Mark G. Steinmetz* and Richard T. Mayes

Contribution from the Department of Chemistry, Marquette University, Milwaukee, Wisconsin 53233. Received February 21, 1984

Abstract: Direct photolysis of 4,4-dimethyl-1,1-diphenyl-1,2-pentadiene (**1**) in *tert*-butyl alcohol yields 1-*tert*-butyl-3,3-diphenylcyclopropene (**2**), $\Phi = 0.0087 \pm 0.0017$, 4,4-dimethyl-1,1-diphenyl-2-pentyne (**3**), $\Phi = 0.0046 \pm 0.0006$, and 1-*tert*-butyl-3-phenylindene (**4**), $\Phi = 0.0112 \pm 0.0014$. Involvement of vinylmethylenes as potential intermediates in **1** photoisomerizations was assessed by independent generation with cyclopropene **2**, the tosylhydrazone **11** of 2,2-dimethyl-5,5-diphenyl-4-pentene-3-one, and 3-*tert*-butyl-5,5-diphenyl-3*H*-pyrazole (**13**). Quantum yields for direct photolysis of **2** were as follows: **1**, $\Phi = 0.050 \pm 0.001$, **4**, $\Phi = 0.096 \pm 0.003$, and 2-*tert*-butyl-3-phenylindene (**5**), $\Phi = 0.023 \pm 0.002$. **1** (3.8%), **2** (19%), and **4** (40%) were products of nitrogen photoextrusion from **13**, and similar results were obtained from the sodium salt **12** of tosylhydrazone **11**. Flash vacuum pyrolysis (FVP) of **2** at 400 °C produced **4** (76%) and 3-*tert*-butyl-1-phenylindene (**15**) (24%). FVP of **4** also gave **15** (26%) and recovered **4** (74%). Allene **1** was recovered in 98% yield after FVP (400 °C). Deuterium labeling of photoproducts was determined for 4,4-dimethyl-1,1-diphenyl-1,2-pentadiene-3-*d*₁ (**1-d**₁); a $\Phi_H/\Phi_D(3) = 3.07$ suggests that the second 1,2-H shift is rate determining as opposed to the small Φ_H/Φ_D of 1.36 for total products, **2** + **3** + **4**, implicating only a low excited-state barrier in the first step. KIEs are derived. Funneling from the singlet excited state to the ground state is suggested for formation of **1** in photolyses of **2**. Discrete ground-state vinylmethylenes adequately account for thermolysis products. Alternative mechanisms are discussed.

The photoisomerization of allene to cyclopropene and methylacetylene was first reported for direct photolyses conducted at 8 K with matrix isolation techniques.¹ We subsequently reported² that conventional solution-phase conditions can be used to effect

comparable photorearrangements of 1,1-diphenylallenes in good yield provided a bulky substituent, i.e., a *tert*-butyl group, is present at C_3 . Otherwise, lower temperatures (−10 °C) have proven effective in suppressing competing dimerization in the case of triphenyl- and tetraphenylallene.³ The generality of allene C_3H_4

(1) Chapman, O. L. *Pure Appl. Chem.* **1975**, 511.

(2) Steinmetz, M. G.; Mayes, R. T.; Yang, J.-C. *J. Am. Chem. Soc.* **1982**, *104*, 3518.

(3) Klett, M. W.; Johnson, R. P. *Tetrahedron Lett.* **1983**, 2523.