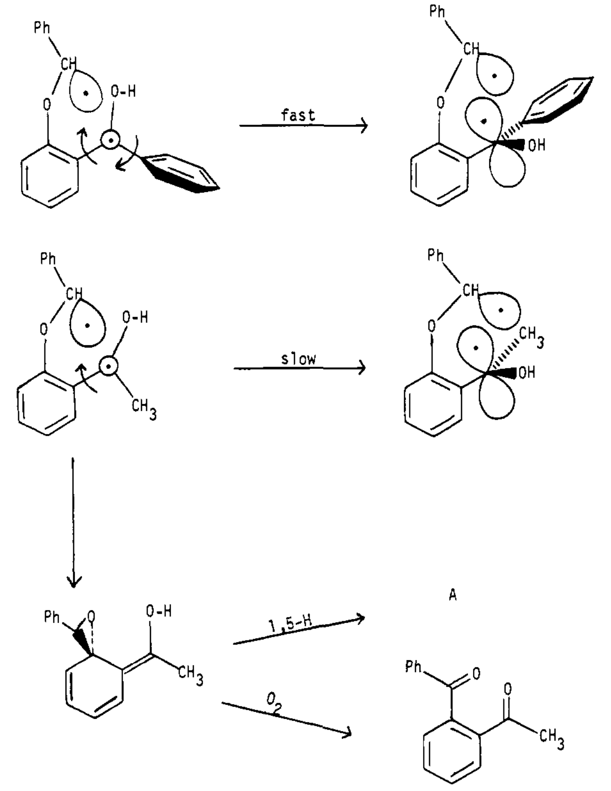
Scheme I



phenone formed from the latter is presumably an oxidation product of the spiro enol. We have not isolated any additional stable products in the case of B. However, the low yields of 4-alkoxy-2-hydroxybenzophenone formed from 4-alkoxy-B[2c] could well be due to oxidation of a spiro enol.

We conclude that A and B differ primarily in the relative rates of the competing biradical processes outlined in Scheme I. The efficiency of benzofuranol formation apparently is directly related to the ease of rotation about the aryl–C_1 bond. Inasmuch as the π-system of a substituted benzoyl group is conjugated in the triplet state, hydrogen abstraction produces a triplet 1,5-biradical with a fully conjugated benzyl radical center. A rotation of approximately 90° is required before cyclization can occur. In the acetophenone-derived biradical, such a rotation reduces the benzylic conjugation and thus is slow. In fact, an EPR study has provided a rate constant of only 10^3 s^{-1} for such a rotation in benzaldehyde ketyl radical.[11] This value may be too small for larger molecules, but the value would not exceed the 10^7 s^{-1} that has been established for rotation about the aryl–carbonyl bond of triplet ketones.[12] In contrast, rotation around one benzyl bond is facile in benzhydryl radicals because compensatory rotation about the other benzyl bond maintains benzylic conjugation. Therefore the B-derived biradical can rapidly rotate into the conformation necessary for cyclization to a furanol. As soon as the biradical becomes a singlet with the proper conformation, it can cyclize rapidly.

The competing spirocyclization does not require rotation about the benzyl bond. The biradical from A has more time than that from B to undergo this reaction, which thus predominates. The reaction could conceivably proceed adiabatically, forming the triplet state of the spiro trienol, although we have no evidence for this possibility. Oxidation of the spiro enol apparently competes with 1,5-sigmatropic hydrogen migration, which can regenerate starting ketone.

Ito, Matsuura, and co-workers have reported large quantum yields for benzocyclobutenol formation from *o*-isopropylbenzophenones[13] and have noted without explanation the very low values that we observed for the corresponding aryl alkyl ketones.[14] We propose that the same conjugative control of bond rotation in biradicals determines cyclization efficiency in both types of reaction. Ito and Matsuura also proposed the intriguing idea that rotation about the benzyl bond may induce the spin–orbit coupling required for intersystem crossing (isc) of the biradical intermediates.[13] This notion of rotation-induced isc has been popular for some time[15] but has not been clearly established as valid for any given system. That rotation may indeed be rate determining for cyclization of our 1,5-biradicals seems to follow from the unusually high efficiency with which B cyclizes. If rotational equilibrium were established before isc, disproportionation of the 1,5-biradical back to starting ketone should be significant.[8] Inasmuch as intersystem crossing determines triplet biradical lifetimes,[16] the very short lifetime for the unsolvated biradical formed from triplet B supports the idea of rotation-induced intersystem crossing.

The ether oxygen atoms make these 1,5-biradicals fully conjugated in the sense that there are p-orbitals on five adjacent atoms. Therefore rotation may have a larger effect on spin–orbit coupling than it does in nonconjugated biradicals. The lifetime-shortening effect of oxygen atoms in 1,4-biradicals may have a similar cause.[17] These ideas are being explored further wth differently substituted ketones.

Acknowledgment. P.J.W. thanks the NSF for continuing support and the John Simon Guggenheim Foundation for a fellowship, which provided the time for this paper. M.A.M. thanks the Chemistry Department of MSU for a L. L. Quill Fellowship. We both thank the NRC of Canada for its hospitality.

Registry No. (*Z*)-**2**, 93254-82-1; (*E*)-**2**, 93254-83-2; (*Z*)-**3**, 93254-84-3; (*E*)-**3**, 93254-85-4; A, 31165-67-0; B, 93254-81-0.

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Stereoselective Substituent Effects on Conrotatory Electrocyclic Reactions of Cyclobutenes

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When cyclobutenes undergo stereospecific conrotatory electrocyclic reactions to form butadienes,[2] substituents at C_3 or C_4 may rotate either "inward" or "outward" (Scheme I). We wish to report experimental results that establish that the energetic preference for substituents at C_3 and C_4 to rotate outward, rather than inward, increases as the π-donor nature of the substituent increases. Theoretical studies reveal a novel electronic origin of this phenomenon.[3]

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[1] (a) Bochum. (b) Pittsburgh.

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Scheme I

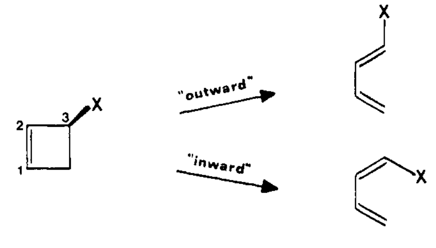

Table I. Activation Parameters for Electrocyclic Reactions of Cyclobutene and Substituted Derivatives

cyclobutenes	log A	E_a, kcal/mol	E_{rel}, kcal/mol
cyclobutene[a]	13.08	32.5	0
3-methylcyclobutene[b]	13.56	31.6	−0.9
cis-3,4-dimethylcyclobutene[c]	13.68	34.0	+1.5
trans-3,4-dimethylcyclobutene	14.01 ± 0.23	30.6 ± 0.4	−1.9
3-chlorocyclobutene	13.07 ± 0.09	29.4 ± 0.2	−3.1
cis-3,4-dichlorocyclobutene	13.87 ± 0.26	35.6 ± 0.5	+3.1
trans-3,4-dichlorocyclobutene	12.96 ± 0.28	25.7 ± 0.4	−6.8
cis-3-chloro-4-methylcyclobutene[d]	12.66 ± 0.06	31.6 ± 0.1	−0.9
3-acetoxycyclobutene	12.58 ± 0.16	27.8 ± 0.3	−4.7
3-ethoxycyclobutene	12.68 ± 0.18	23.5 ± 0.3	−9.0
cis-3,4-diethoxycyclobutene	12.89 ± 0.26	27.8 ± 0.4	−4.7
cis-3,4-dimethoxycyclobutene	13.25 ± 0.39	28.6 ± 0.6	−3.9
cis-3-chloro-4-methoxycyclobutene[e]	12.85 ± 0.13	29.1 ± 0.3	−3.4
cis-3-methoxy-4-methylcyclobutene[d]	11.71 ± 0.35	25.5 ± 0.6	−7.0

[a] Copper, W.; Walters, W. D. *J. Am. Chem. Soc.* **1958**, *80*, 4220. [b] Frey, H. M.; Marshall, D. C. *Trans. Faraday Soc.* **1965**, *61*, 1715. [c] Srinivasan, R. *J. Am. Chem. Soc.* **1969**, *91*, 7557. [d] Methyl rotates inward. [e] Chloro rotates inward.

Table II. Influence of 3- or 4-Substituents upon Activation Energies for Conrotatory Electrocyclic Reactions of Cyclobutenes

substituent	direction of rotation	
	outward	inward
Me	−1	+3
Cl	−3	+6
OAc	−5	
OR	−9	+5

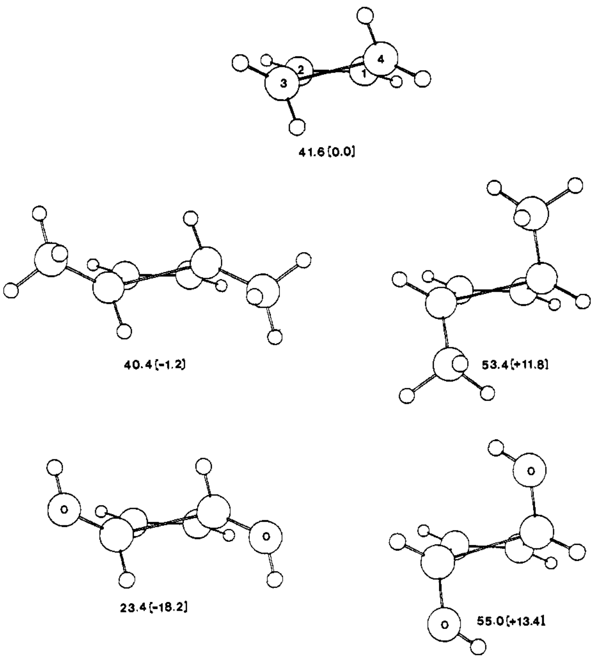

Figure 1. Transition structures for the conrotatory electrocyclic reactions of cyclobutene, *trans*-3,4-dimethylcyclobutene, and *trans*-3,4-dihydroxycyclobutene. Each view is along the C_2 axis of symmetry, with the breaking C_3–C_4 bond toward the observer. Calculated 3-21G activation energies in kcal/mol are given below each figure with relative activation energies in brackets.

Table I shows the activation parameters found for the thermolysis of cyclobutene and substituted cyclobutenes, including 11 new examples. Thermolysis of the labile 3-ethoxycyclobutene was carried out at 30–50 °C, and the reaction was followed by UV in hexane or by NMR in CCl_4 solution. All other data are for gas-phase reactions, which were followed by GC analysis. As shown in Table I, substitution mainly influences the activation energies, while log A values change only slightly.

Frey and co-workers found that the effects of alkyl subsituents at C_3 and C_4 on the rates of conrotatory electrocyclic opening of cyclobutenes are approximately additive.[5] The data in Table I indicate that the additivity of substituent effects hold approximately for a wider range of substitution patterns. The substituent effect on the activation energy for outward rotation is obtained from the difference between the E_a for cyclobutene and that for a 3-substituted cyclobutene or from the difference between E_a for a 3-substituted and that for a trans-3,4-disubstituted cyclobutene. The difference between the E_a for 3-substituted cyclobutenes and cis-3,4-disubstituted cyclobutenes, where one group rotates inward, gives substituent effects for inward rotations. Table II summarizes the substituent effects upon activation energies for outward or inward rotation of several substituents. It is apparent that the substituent preference for outward rotation decreases along the series, OR > Cl > CH_3. Outward reaction of an alkoxy substituent is 14 kcal/mol easier than inward rotation! This trend is opposite to expectation based upon steric control of the direction of ring opening.[6] In 1980, Curry and Stevens found that the larger alkyl group in 3-methyl-3-alkylcyclobutenes sometimes rotates inward. These authors postulated that the better donor preferentially rotates outward.[7] A dramatic example of this was recently reported by Dolbier et al.[8] Perfluoro-*trans*-3,4-dimethylcyclobutene opens to form the more crowded product arising from inward rotations of the two bulky trifluoromethyl groups. The activation energy for this process is 19.2 kcal/mol lower than that for the opposite conrotatory electrocyclization, which involves outward rotation of these trifluoromethyl groups.[8]

In order to elucidate the origin of these subsitutent effects, we have studied theoretically the conrotatory electrocyclic reactions of cyclobutene, *trans*-3,4-dimethylcyclobutene, and *trans*-3,4-dihydroxycyclobutene.[9] The geometries of reactants, transition

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(4) Synthesis: *trans*-3,4-dimethylcyclobutene (Winter, R. E. K. *Tetrahedron Lett.* **1965**, 1207), *cis*-3,4-dichlorocyclobutene (Pettit, R.; Henery, J. *J. Org. Synth.* **1970**, *50*, 36), *trans*-3,4-dichlorocyclobutene (Hoberg, H.; Frohlich, C. *Synthesis* **1981**, 830), and 3-acetoxycyclobutene (Wiberg, K. B.; Williams, V. Z.; Friedrich, L. E. *J. Am. Chem. Soc.* **1970**, *92*, 564) were prepared according to established procedures. 3-Chlorocyclobutene was obtained by partial reduction of *cis*-3,4-dichlorocyclobutene with tri-*n*-butyltin hydride (65%). S_N2' reactions of *cis*-3,4-dichlorocyclobutene with alkoxides (Kirmse, W.; Scheidt, G.; Vater, H. J. *J. Am. Chem. Soc.* **1978**, *100*, 3945) afforded *cis*-3-chloro-4-methoxycyclobutene, *cis*-3,4-dimethoxycyclobutene, and *cis*-3,4-diethoxycyclobutene. Similarly, *cis*-3-chloro-4-methylcyclobutene was obtained from *cis*-3,4-dichlorocyclobutene and methyl lithium (57%), and *cis*-3-methoxy-4-methylcyclobutene was obtained from *cis*-3-chloro-4-methoxycyclobutene and methyl lithium (24%). Elimination of hydrogen chloride from 1-chloro-3-ethoxycyclobutene (Sieja, J. B. *J. Am. Chem. Soc.* **1971**, *93*, 130) (potassium *tert*-butoxide, 25 °C, continuous distillation of product at 10 mm) afforded 3-ethoxycyclobutene. R. Hummerich, K. Friedrich, K. W. Kempf, H. J. Klocke, F. Scheidt, R. Thole, and H. J. Vater contributed to the preparative and kinetic work carried out at Bochum.

(5) Frey, H. M.; Pope, B. M.; Skinner, R. F. *Trans. Faraday Soc.* **1967**, *63*, 1166.

(6) The sizes, measured by A values, of substituents are 1.7, 0.7, 0.7, and 0.4 for Me, OR, OAc, and Cl, respectively: Eliel, E. L.; Allinger, N. L.; Angyal, S. J.; Morrison, G. A. "Conformational Analysis"; Wiley-Interscience: New York, 1965; p 44.

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

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

(9) The symmetry of disubstituted molecules resulted in computational savings.

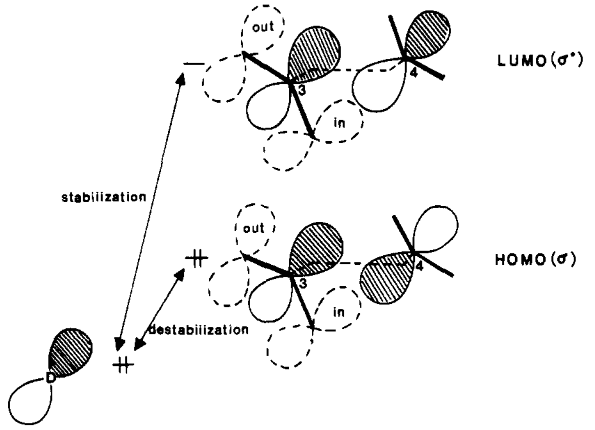

Figure 2. HOMO and LUMO of the cyclobutene transition structure and the occupied p orbital of a donor orbital. The positions that a donor substituent orbital assumes upon inward or outward rotation are shown by the dashed lines.

structures, and products were fully optimized at the RHF level using the 3-21G basis set[10] and analytical energy gradients.[11] The transition structures and calculated activation energies are shown in Figure 1.[12] The transition structure for the cyclobutene–butadiene interconversion agrees closely to that obtained by Breulet and Schaefer at a higher level.[13] The activation energy at the 3-21G level is 9 kcal/mol too high (7.6 kcal/mol with zero-point energy corrections) but becomes only 0.3 kcal/mol too high when MP2 correlation energy corrections are made. The 3-21G activation energies for the other reactions in Figure 1 are all about 10 kcal/mol too high as compared to experimental data or to estimates based upon the substituent additivities given in Table II (with hydroxy used as a model for alkoxy). This error is due to the neglect of correlation energy, which stabilizes the transition structures more than the reactants and is similar to that found in 3-21G calculations on sigmatropic shifts.[14]

The large difference between the activation energies for the outward and inward rotations of hydroxy groups in *trans*-3,4-dihydroxycyclobutene is not a result of steric repulsion upon inward rotation but can be understood by examining the interactions between the frontier molecular orbitals of the cyclobutene transition structure and the occupied p orbital of a donor substitutent. In the transition structure for a conrotatory electrocyclization, the HOMO of cyclobutene is essentially a distorted σ orbital, while the LUMO is a σ^* orbital.[15] These are sketched in Figure 2. Upon outward rotation of a donor substituent, the donor orbital can mix with the LUMO, resulting in stabilization and lowering of the activation energy. This is only partially counteracted by the destabilizing four-electron interaction of the donor orbital with the distorted cyclobutene HOMO. Because of the location of the donor orbital upon outward rotation (shown by the dashed lines labeled "out"), the donor orbital overlaps primarily with the atomic orbital at C_3.

Upon inward rotation, the donor orbital will move into the location marked by the dashed orbital labeled "in". In this location the donor orbital overlaps with the atomic orbitals at both C_3 and C_4. The interaction of an inwardly rotating donor orbital with the distorted cyclobutene LUMO is less than that of an outwardly rotating donor orbital, because the signs of the neighboring lobes of the atomic orbitals at C_3 and C_4 are opposite. Consequently, stabilization upon inward rotation of the donor is less than upon outward rotation. At the same time, the donor orbital overlaps more with the distorted cyclobutene HOMO upon inward rotation than upon outward rotation, due to overlap at both C_3 and C_4. This destabilizing interaction is larger for inward rotation than outward rotation. Thus, both interactions favor outward rotation, and the extent of this preference depends upon the donor ability of the substituent. With π-acceptor substituents, orbital interactions also occur between the HOMO of cyclobutene and the empty orbital of the acceptor. This two-electron stabilizing interaction is maximized when the acceptor rotates inward and may cause acceptors to preferentially rotate inward. Experimentally, acceptors show little preference for inward and outward rotation.[2]

Substituent effects of this type should influence other pericyclic reactions, such as disrotatory 6π-electron electrocyclizations, and may influence the overall stereochemistry of isomerizations of cyclopropanes[16] and related molecules.

Acknowledgment. We are grateful to the National Science Foundation for financial support of this research, to the Alexander von Humboldt Foundation for a U.S. Senior Scientist Award to K.N.H., which made this collaboration possible, and to Professor William R. Dolbier for enlightening discussions.

Registry No. Cyclobutene, 822-35-5; 3-methylcyclobutene, 1120-55-4; *cis*-3,4-dimethylcyclobutene, 1517-14-2; *trans*-3,4-dimethylcyclobutene, 1517-13-1; 3-chlorocyclobutene, 93280-82-1; *cis*-3,4-dichlorocyclobutene, 2957-95-1; *trans*-3,4-dichlorocyclobutene, 1192-02-5; *cis*-3-chloro-4-methylcyclobutene, 93280-83-2; 3-acetoxycyclobutene, 27238-02-4; 3-ethoxycyclobutene, 93280-84-3; *cis*-3,4-diethoxycyclobutene, 93280-85-4; *cis*-3,4-dimethoxycyclobutene, 67520-63-2; *cis*-3-chloro-4-methoxycyclobutene, 67520-62-1; *cis*-3-methoxy-4-methylcyclobutene, 93280-86-5; methyllithium, 917-54-4; 1-chloro-3-ethoxycyclobutane, 93280-87-6.

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(12) A full paper will give details of these and additional calculations.

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Novel Polyelectrolyte Composites That Yield Polycationic Electrode Coatings with Large Ion Exchange Capacities and Exceptionally High Effective Diffusion Coefficients for Incorporated Counterions

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The use of adherent polyelectrolytes to bind counterionic reactants to electrode surfaces has grown in popularity since this tactic was first demonstrated with poly(4-vinylpyridine).[1] Despite the variety of reports in which polyelectrolyte-coated electrodes have been exploited,[2-4] the number of polyelectrolytes suitable for preparing stable electrode coatings remains relatively small. Most commonly available ionic polymers are either too soluble or undergo facile counterion exchange so that incorporated ionic reactants are rapidly lost from electrode coatings.

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[⊥] Contribution No. 7089.

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