Table III. Stereochemistry of Addition of Olefins to Benzyne

Olefin, RC=CR′	% retention of stereochemistry in cycloadduct
R = Me, R′ = OEt (cis)	94^{b}
R = Me, R′ = OMe (cis)	88^{c}
R = Me, R′ = OAc (cis)	82^{c}
R, R′ = Cl (cis)	68^{d}
R = Me, R′ = OEt (trans)	$79^{a,b}$
R = Me, R′ = OMe (trans)	$51^{a,c}$
R = Me, R′ = OAc (trans)	$67^{a,c}$
R, R′ = Cl (trans)	81^{d}

[a] High component of ene reaction. [b] H. H. Wasserman, A. J. Solodar, and L. S. Keller, *Tetrahedron Lett.*, 5597 (1968). [c] L. Friedman, R. J. Osiewicz, and P. W. Rabideau, *ibid.*, 5735 (1968). [d] Reference 42.

been shown to proceed in the manner predicted by standard orbital symmetry considerations[42] and does not need any discussion since the situation is quite analogous to the situation of $4_\pi + 2_\pi$ cycloaddition of a diene and an olefin.

Conclusion

In this work, we have provided arguments in order to show the following.

(a) Correlation diagrams can provide the framework for a detailed analysis of the effect of the electronic properties of the reagents upon the stereoselectivity of the cycloaddition reaction. Correlation diagrams allow for the recognition of the importance of configuration interaction in the cases of cycloadditions involving reagents of widely different ionization potential and electron affinity. In this respect, our treatment constitutes an extension of the Woodward–Hoffmann and Longuet-Higgins–Abrahamson treatment.

(b) Non least motion processes can occur whenever configuration interaction is unimportant, while least motion processes can uniformly become allowed whenever configuration interaction becomes important.

(c) Both the stereoselectivity and nonstereoselectivity of different types of cycloadditions can be the result of concerted mechanisms. This implies that the mechanism of many reactions which were previously thought to proceed *via* the intermediacy of diradical or dipolar species either because they were nonstereoselective or because they proceed by a symmetry non-allowed manner has to be reexamined in the light of our findings.

We regard the conclusions reported here as significant and it is important to single out the workers who have expressed ideas related to ours. In this respect, the possibility of concerted $2_s + 2_s$ cycloaddition of singlet oxygen and electron rich olefins has been discussed by Kearns.[43] Furthermore, Jackson[34] has considered the activation energy of four-center forbidden reactions and implied that enhanced polarity of the transition state can lower the activation energy of such reactions. Finally, the calculations of Raff and Porter[35] mentioned before have beautifully illustrated the importance of configuration interaction in reducing the forbiddeness of $2_\sigma + 2_\sigma$ cycloadditions.

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[42] M. Jones, Jr., and R. H. Levin, *J. Amer. Chem. Soc.*, **91**, 6411 (1969).

[43] D. R. Kearns, *ibid.*, **91**, 6559 (1969).

Configuration Interaction and Organic Reactivity.
II. Electrocyclic Reactions

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Abstract: The effect of substituents on the stereochemistry of electrocyclic reactions is examined with the aid of perturbation theory at the one-electron level. It is shown that increasing substitution by either electron-releasing or electron-withdrawing groups tends to reverse the stereoselectivity of electrocyclic reactions. The effect of configuration interaction on the stereoselectivity of electrocyclic reactions is examined by an orbital symmetry approach. It is shown that configuration interaction can also give rise to reversal of the stereoselectivity of electrocyclic reactions especially when the system undergoing ring closure or ring opening is asymmetically substituted by electron-releasing and electron-withdrawing groups.

We have seen that configuration interaction is all important in determining the stereoselectivity of cycloaddition reactions.[2] We now would like to extend these ideas to the case of electrocyclic ring closures. We shall use two approaches in order to demonstrate that substituents can effect the preference for conrotatory or disrotatory ring closure in conjugated systems. First, we shall use a simple perturbation treatment[3] in order to make predictions regarding the stereoselectivity of ring closures. Subsequently, we shall use an orbital symmetry approach[4] and show how configuration interaction can affect the preference for conrotation or disrotation in representative systems.

It is important to realize that ring closures can be viewed as intramolecular cycloadditions. For example, the ring closures of butadiene and hexatriene can be viewed as intramolecular 2 + 2 and 4 + 2 cycloadditions. One can derive stereoselection rules for ring closures in a very simple manner by assum-

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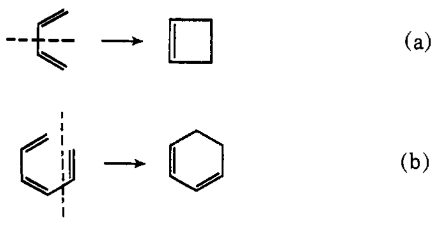
[2] N. D. Epiotis, *J. Amer. Chem. Soc.*, **95**, 1191 (1973).

[3] M. J. S. Dewar, "The Molecular Orbital Theory of Organic Chemistry," McGraw-Hill, New York, N. Y., 1969.

[4] R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry," Academic Press, New York, N. Y., 1970; H. C. Longuet-Higgins and E. W. Abrahamson, *J. Amer. Chem. Soc.*, **87**, 2045 (1965).



ing that the two ethylene segments in butadiene can be treated as two isolated ethylenes and that the butadiene and ethylene segments of hexatriene can be treated as isolated butadiene and ethylene. Of course, any rules derived on the basis of such a model will be reliable only to the extent that the assumption of negligible interaction between individual double bonds within a polyene is reliable.[5] Stereoselection rules can be simply derived by considering the HOMO–LUMO interactions of the two formal ethylenes in the case of butadiene ring closure and the HOMO–LUMO interactions of the formal butadiene and ethylene in the case of hexatriene ring closure. These interactions are shown in Figure 1 and lead to predictions which are identical with the predictions of Woodward and Hoffmann.[4] Accordingly, one might expect that the effect of substitution upon the stereoselectivity of ring closures will resemble the effect of substitution on the stereoselectivity of intermolecular cycloadditions. While this expectation is valid, one would have to note an important difference between ring closures and intermolecular cycloadditions. Specifically, in the case of ring closures steric effects are comparable for both types of ring closures, while in the case of intermolecular cycloadditions steric effects are extremely different for the two types of cycloaddend union. In the case of ring closures, one cannot differentiate between least motion and non least motion paths since both conrotation and disrotation involve the same amount of electronic motions. On the other hand, in the case of intermolecular cycloadditions one can distinguish between least motion and non least motion paths, the former involving s + s union of the cycloaddends and the latter involving s + a union of the cycloaddends. On the basis of these considerations, one can reasonably expect that the stereoselectivity of ring closures will primarily depend on electronic effects because in ordinary cases the steric constraints imposed upon conrotation and disrotation are similar or can be made to be similar by appropriate design of the molecule to be investigated. This situation is quite unlike the situation in intermolecular cycloadditions where stereoselectivity is determined jointly by steric and electronic effects. In our subsequent discussions, we shall be concerned with the effect of substituents on the electronic preference for conrotatory or disrotatory ring closure.

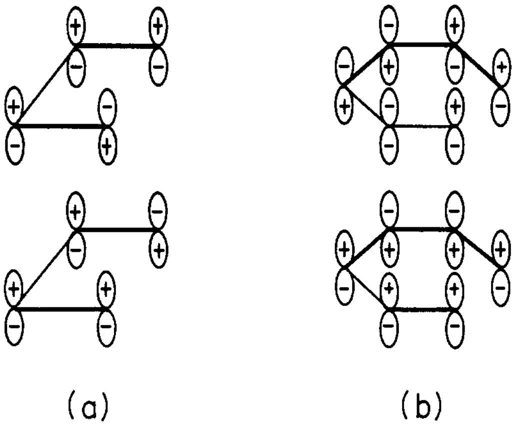


Figure 1. Orbital interactions determining stereoselection of electrocyclic reactions: (a) intramolecular 2 + 2 cycloaddition, (b) intramolecular 4 + 2 cycloaddition.

Theory

We shall begin with a simple perturbation analysis of ring-closure reactions. The interaction of the uniting p orbitals of the conjugated system undergoing ring closure gives rise to a stabilization energy which can be approximately evaluated by a simple application of first-order perturbation theory. Second-order effects will be much smaller in magnitude and can be neglected for the sake of simplicity. According to first-order perturbation theory, the stabilization energy derived from the interaction of two orbitals of the same energy, or, in our case two p orbitals belonging to the same MO, is given by the expression

$$(\mathrm{se})_i = n_i c_i c_i'\gamma \tag{1}$$

where n_i denotes the number of electrons occupying the ith MO of the conjugated system, c_i and c_i' are the coefficients of the uniting p orbitals belonging to the ith MO, and γ is the resonance integral of the uniting p orbitals. The total stabilization energy is given by the expression

$$\mathrm{SE} = \sum_{i=1}^{j} (\mathrm{se})_i = \sum_{i=1}^{j} n_i c_i c_i'\gamma \tag{2}$$

The value of SE will be maximal under the following two conditions: (a) $\sum_{i=1}^{j} n_i c_i c_i'$ is a negative quantity, γ is a negative quantity, and the mode of ring closure is conrotatory; (b) $\sum_{i=1}^{j} n_i c_i c_i'$ is a positive quantity, γ is a positive quantity, and the mode of ring closure is disrotatory. The theoretical analysis provided above leads to the same predictions as the Woodward–Hoffmann rules and is similar to the theoretical analysis provided by Fukui.[6] On the basis of our formulation, substituent effects can now be discussed in terms of the variation of SE which accompanies substitution of the conjugated system undergoing ring closure.

Linear Even Polyenes. We shall first consider the case of ring closure of a linear even polyene substituted by an electron donating group. According to perturbation theory, the interaction of the electron donating substituent with the LUMO of the polyene results in charge transfer from the highest occupied orbital of the substituent to the LUMO of the polyene. The expression for the stabilization energy upon ring closure of such a substituted system becomes

$$\mathrm{SE} = \sum_{i=1}^{j} n_i c_i c_i'\gamma + k c_{j+1} c_{j+1}'\gamma \tag{3}$$

In the case of interest we have

$$c_{j+1} c_{j+1}' = -c_j c_j' \tag{4}$$

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(5) M. J. S. Dewar and H. N. Schmeising, *Tetrahedron*, **11**, 96 (1960), and references therein.

(6) K. Fukui, *Tetrahedron Lett.*, 2069 (1965).

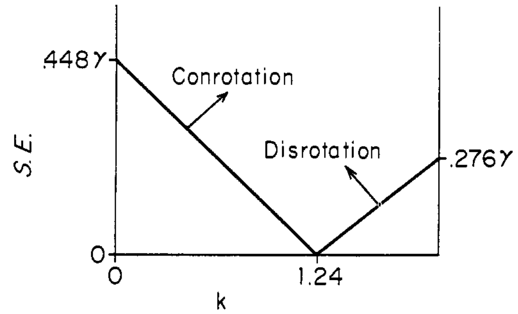
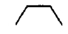
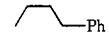
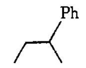
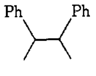
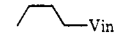
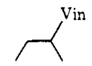
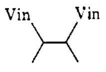


Figure 2. The variation of SE for conrotatory and disrotatory ring closure of butadiene as a function of k, the charge transferred to the LUMO or removed from the HOMO of butadiene under the influence of donor or acceptor substituents, respectively.

Table I. Substituent Effects on the Stabilization Energy for Conrotatory Ring Closure of Butadiene[a]

Substrate	Stabilization energy, γ
	0.448
	0.398
	0.352
	0.414
	0.392
	0.388
	0.332
	0.406
	0.376

[a] Ph = phenyl, Vin = vinyl.

and eq 3 can be rewritten

$$\mathrm{SE} = \sum_{i=1}^{j} n_i c_i c_i' \gamma - k c_j c_j' \gamma \tag{5}$$

Similarly the interaction of an electron accepting group with the HOMO of the polyene results in charge transfer from the HOMO of the polyene to the lowest unoccupied orbital of the electron accepting substituent. The expression for the stabilization energy upon ring closure of such a substituted system becomes

$$\mathrm{SE} = \sum_{i=1}^{j} n_i c_i c_i' \gamma - k c_j c_j' \gamma \tag{6}$$

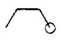
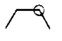
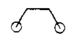
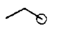
In the previous expressions, k stands for the number of electrons which are transferred from the highest occupied orbital of the substituent to the LUMO of the conjugated system or from the HOMO of the conjugated system to the lowest unoccupied orbital of the substituent.

On the basis of eq 5 and 6, the general conclusion is reached that increasing substitution of a linear even polyene by either electron-donating or electron-accepting substituents will give rise to a progressive decline of the stabilization energy for the preferred mode of ring closure and will ultimately give rise to a preferential mode or ring closure which is opposite to the one predicted for the unsubstituted molecule. Figure 2 shows how SE varies with k in the case of butadiene ring closure. In terms of our theory, the value of k is a function of the strength of interaction between any substituent and butadiene as well as the number of substituents on butadiene and increases as either or both of these variables increases.

These general predictions have been tested by actual calculations. We have used Hückel wave functions[7] of vinyl- and phenyl-substituted butadienes and calculated the stabilization energy for conrotatory ring closure according to eq 2. The results are shown in Table I and are in agreement with the general conclusions stated above. It can be seen that increased substitution by vinyl and phenyl groups progressively diminishes the stabilization energy for conrotatory ring closure. It can also be seen that in agreement with theoretical expectations the effect of substitution is greater at C-1 than at C-2. This occurs because the interaction of the substituent with the HOMO and LUMO of butadiene is greater at C-1 than at C-2 simply because the atomic orbital coefficients of the HOMO and LUMO of butadiene are greater for the C-1 than for the C-2 atomic p orbital.

Since this treatment ignores the inductive effect of the substituents upon the MO's of butadiene, we have also investigated the effect of varying the Coulomb integral of C-1 and C-2 on butadiene upon the stabilization energy of conrotatory ring closure. The results are shown in Table II and indicate that decreasing the Coulomb integral of C-1 or C-2 through attachment of a substituent progressively diminishes the stabilization energy for conrotatory ring closure. It is well known that both π-donor and π-acceptor substituents decrease the Coulomb integral of the carbon atom where they are attached.[8] Thus, it is clear that both the conjugative and inductive effect of a substituent will act as to reduce the stabilization energy for conrotatory ring closure in butadiene and can ultimately give rise to a preferred mode of ring closure which is opposite to the one predicted for the unsubstituted molecule.

Table II. Dependence of the Stabilization Energy for Conrotatory Ring Closure on the Magnitude of the Coulomb Integrals of Substituted Carbon Centers[a]

Molecule	Coulomb integral		
	α	$\alpha + 1\beta$	$\alpha + 2\beta$
	0.448	0.366	0.258
	0.448	0.412	0.344
	0.448	0.344	0.192
	0.500	0.388	

[a] All stabilization energies are in units of γ. Carbon atom of variable Coulomb integral is indicated by circle.

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(7) A. Streitwieser and J. I. Brauman, "Supplemental Tables of Molecular Orbital Calculations," Pergamon Press, New York, N. Y., 1965.

(8) For a discussion of the effect of heteroatoms on the MO properties of conjugated systems, see A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists," Wiley, New York, N. Y., 1961.

Linear Odd Systems. We shall first consider the case of ring closure of a linear odd system substituted by an electron donating group. According to perturbation theory, the interaction of the electron donating substituent with the LUMO of the odd system results in charge transfer from the HOMO of the substituent to the LUMO of the odd system. Of course, this necessitates that the substituent is not attached on a carbon atom which is located on a nodal surface of the LUMO of the odd system. The expression for the stabilization energy upon ring closure of such a substituted system becomes

$$\mathrm{SE} = \sum_{i=1}^{j} n_i c_i c_i' \gamma + k c_{j+1} c_{j+1}' \gamma \qquad (3')$$

Similarly, the interaction of an electron accepting group with the HOMO of the odd system results in charge transfer from the HOMO of the odd system to the LUMO of the electron acceptor substituent. Again this necessitates that the substituent is not attached to a carbon atom which is located on a nodal surface of the HOMO of the odd system. The stabilization energy upon ring closure of such a substituted system is given by

$$\mathrm{SE} = \sum_{i=1}^{j} n_i c_i c_i' \gamma - k c_j c_j' \gamma \qquad (6')$$

As in the previous case, the general conclusion is reached that increasing substitution of an odd system by electron-donating or electron-accepting groups will give rise to a progressive decline of stabilization energy of the mode of ring closure defined for the unsubstituted system; *e.g.*, increased substitution of butadiene can lead to disrotatory ring closure while increased substitution of trimethylene can lead to disrotatory ring closure. These general predictions have been tested by actual calculations. By using Hückel wave functions of various vinyl and phenyl substituted trimethylenes, we have calculated the stabilization energy for conrotatory ring closure according to eq 2. In these calculations we have used the heteroatom model[9] and assumed that trimethylene is electronically equivalent to the allyl anion. The results of these calculations are shown in Table III and are in agreement with the general conclusions stated above. It can be seen that increasing substitution by electron-donating and electron-accepting groups progressively diminishes the stabilization energy for conrotatory ring closure. Both vinyl and phenyl groups act mainly as acceptors and it can be seen that they have no effect when placed at the middle carbon of trimethylene since there is a node through the middle carbon in the HOMO of trimethylene.

The inductive effect of a substituent upon the stabilization energy of conrotatory ring closure in trimethylene has been ascertained by calculations and it was found that decreasing the Coulomb integral of a carbon atom in trimethylene leads to decreasing stabilization energy for conrotatory ring closure. The results are shown in Table II and it is concluded that both the conjugative and inductive effects of substituents lead to a lowering of the stabilization energy for conrotatory ring closure in trimethylene.

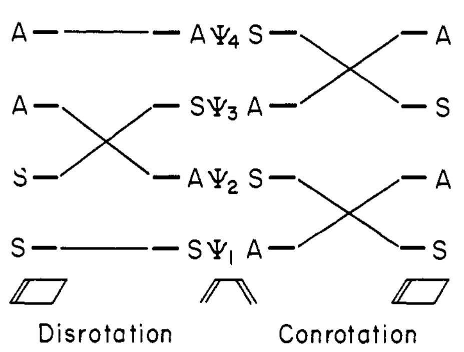
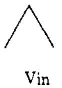
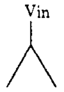
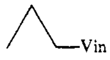
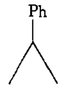


Figure 3. Correlation diagrams for disrotatory and conrotatory transformation of butadiene to cyclobutene.

Table III. Substituent Effects on the Stabilization Energy for Conrotatory Ring Closure of Trimethylene[a]

Substrate	Stabilization energy, γ
	0.500
	0.500
	0.332
	0.252
	0.500
	0.282

[a] Ph = phenyl, Vin = vinyl.

In summary, we conclude that increased substitution will lead to increased probability of a ring closure occurring by the opposite mode to the one predicted for the unsubstituted system.

Configuration Interaction. Configuration interaction can modify results obtained by such one-electron perturbation approaches. The case of butadiene ring closure will be used illustratively and the theoretical framework will again be the Woodward–Hoffmann orbital symmetry correlation approach. Figure 3 shows the well-known correlation diagrams for conrotatory and disrotatory ring closures of butadiene. It is obvious that reversal of the stereoselectivity of butadiene ring closure can be accomplished if one promotes two electrons from ψ_2 to ψ_3 of butadiene. It is then obvious that the importance of configuration interaction will become increasingly significant as the energy gap separating ψ_2 and ψ_3 is decreased. As the energy of ψ_2 and ψ_3 converges to a single value, the ground state and the diexcited configuration of butadiene will mix to an increasing extent and progressively make disrotation allowed. We shall now examine the substitution patterns which most effectively lead to decreased energy separation of ψ_2 and ψ_3 of butadiene.

A. Nonpolar (AD) Substitution. Substitution patterns of the type shown below lead to decreasing energy

(9) F. A. Matsen, *J. Amer. Chem. Soc.*, 72, 5243 (1950).

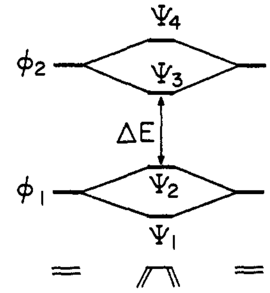
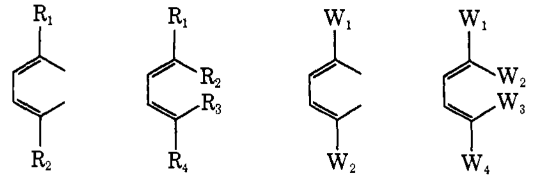


Figure 4. Derivation of butadiene MO's from the MO's of ethylene.

separation of ψ_2 and ψ_3 in butadiene. This can be understood very simply by considering the hypothetical union of two ethylenes to form butadiene. This is shown in Figure 4, and it is immediately obvious that the energy separation ΔE in butadiene is a function of the energy separation of ϕ_1 and ϕ_2 in the ethylene components. In particular, as the energy separation of ϕ_1 and ϕ_2 in the ethylene components decreases, then ΔE in butadiene is also expected to decrease. Now, it is well known that donor and acceptor substituents give rise to a decrease in the energy gap between ϕ_1 and ϕ_2 of an ethylene. This has been discussed theoretically and verified experimentally. The bathochromic shift of the lowest π,π^* transition of ethylene which accompanies substitution of the ethylene constitutes a pertinent example.[10] It is then expected that symmetrically substituted butadienes will exhibit an energy separation between ψ_2 and ψ_3 which is smaller than in the case of unsubstituted butadiene. The data shown in Table IV illustrate the validity of these simple predictions. We conclude that configuration interaction will be more important in nonpolarly substituted butadienes than in butadiene itself.



R_1, R_2, R_3, R_4 = electron donating groups
W_1, W_2, W_3, W_4 = electron accepting groups

Table IV. Effect of Nonpolar 1,4-Substitution of Butadiene on the Lowest Singlet π,π^* Transition[a]

Substituents		λ_{max}, nm	
R_1	R_2	EtOH	Gas
H	H		217
CH_3	CH_3		218[b]
Cl	Cl		243[b]
$COOCH_3$	$COOCH_3$	260[b]	

[a] T. Fueno and K. Yamaguchi, *J. Amer. Chem. Soc.*, **94**, 1119 (1972). [b] Average of geometric isomers.

B. Polar (AX) Substitution. Substitution patterns of the type shown below can lead to very significant decrease of the energy separation of ψ_2 and ψ_3 in butadiene. This can be very simply understood by reference to Figure 5. In particular, the staggering of the energy levels of the two ethylene components can lead to a small energy gap separating ψ_2 and ψ_3 in the composite butadiene. The data of Table V show some results which are in agreement with these simple predictions. We conclude that configuration interaction will be extremely important in polarly substituted butadienes.

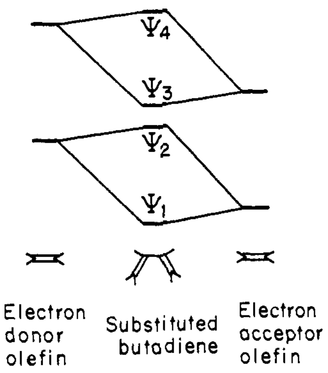


Figure 5. Derivation of the MO's of a polarly substituted butadiene.

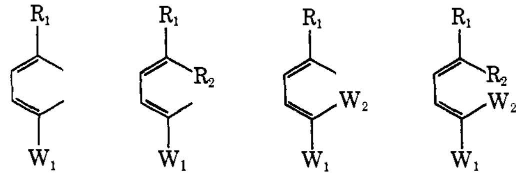


Table V. Effect of Polar 1,4-Substitution of Butadiene on the Lowest Singlet π,π^* Transition[a]

Substituents		λ_{max}, nm	
R_1	R_2	Gas	*n*-Hexane
H	H	217	
CN	H	229[b]	240[b]
CN	CH_3	237[b]	250[b]
$COOCH_3$	H	233[b]	244[b]
$COCH_3$	CH_3	255[b]	268[b]

[a] T. Fueno and K. Yamaguchi, *J. Amer. Chem. Soc.*, **94**, 1119 (1972). [b] Average of geometric isomers.

C. Heteroatom Substituted Butadienes. Heterobutadienes exhibit reduced energy separation of ψ_2 and ψ_3. The situation is similar to the previous cases and has been discussed before.[11] Accordingly, configuration interaction will be more important in heterobutadienes than butadiene itself.

We have seen that a one-electron approach to the problem of the stereoselectivity of ring closures leads to the conclusion that substitution will lead to an increased preference for a ring-closure mode which is opposite to the one predicted for the unsubstituted system. The recognition of the importance of configuration interaction allows one to make more detailed predictions. Specifically, configuration interaction dictates that both nonpolar (AD) and polar (AX) substitution will tend to reduce the stabilization energy difference between two modes of ring closure and that polar substitution will be more effective in accomplishing this. The situation is exactly analogous electronically to the situation in intermolecular cycloadditions. For

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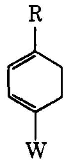
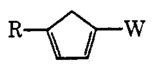
(10) K. Higashi, H. Baba, and A. Rembaum, "Quantum Organic Chemistry," Interscience, New York, N. Y., 1965, and references therein.

(11) H. H. Jaffé and M. Orchin, "Theory and Applications of Ultraviolet Spectroscopy," Wiley, New York, N. Y., 1962.

example, ring closures of nonpolarly substituted butadienes will be intramolecular AD 2 + 2 cycloaddition while ring closures of polarly substituted butadienes will be intramolecular AX 2 + 2 cycloadditions. Similarly ring closures of nonpolarly substituted hexatriene will be intramolecular AM 4 + 2 cycloadditions while ring closures of polarly substituted butadienes will be intramolecular AX 4 + 2 cycloadditions.

We emphasize again that unlike the case of intramolecular cycloaddition, electrocyclic ring closures are primarily subject to electronic effects. Accordingly, it is expected that an actual reversal of the stereoselectivity predicted for the unsubstituted molecule can only obtain if the substituents are many and appropriately oriented. However, a convenient way of testing and predicting would be to examine systems which are constrained to ring close by only one stereochemical mode. Systems of this type can be suitable substrates for investigating the effect of substituents in removing the forbiddenness of a stereochemical ring closure mode.



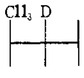
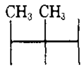
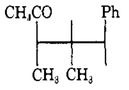
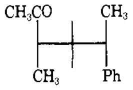
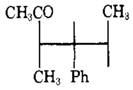


Discussion

The stereochemical course of ring opening and ring closure reactions has been a target of numerous theoretical investigations.[12-14] In this work, we analyzed in a qualitative manner the effect of substituents on the energy difference between two stereochemical modes of ring opening and ring closing. We saw that substituents tend to reduce this energy difference and this conclusion was based on both a one-electron treatment and a treatment which allowed for the recognition of the importance of configuration interaction. It is interesting that the importance of configuration interaction in modifying the stereochemical preference of electrocyclic reactions in even the case of an unsubstituted substrate has in a sense been demonstrated by calculations. Thus, valence bond estimates favor conrotation over disrotation by 100 kcal/mol in the case of the transformation of cyclobutene to butadiene.[14] On the other hand, configuration interaction calculations using SCF wave functions favor conrotation over disrotation only by about 13 kcal/mol in the same system.[12] However, this difference in the two estimates might not be due only to the effect of configuration interaction but also to differences in the parametrization and the general quality of the two calculations.

There have been no studies carried out with the explicit purpose of elucidating the effect of substituents on electrocyclic reactions. However, there is already some indicative evidence which seems to be relevant to the concepts outlined in this paper. The best example is the stereochemistry of ring closure of trimethylene which appears to be conrotatory in the absence of substituents and disrotatory when multisubstitution of the trimethylene obtains. Some pertinent results are shown in Table VI. This puzzling behavior of substituted trimethylene may be a consequence of the electronic effect of the substituents. Hoffmann[15] has calculated by the extended Hückel method the energies of the symmetric (S) and antisymmetric (A) nonbonding orbitals of trimethylene in its equilibrium geometry and found that the A level is lower in energy than the S level by 0.55 eV. He also found that the energy ordering of the S and A levels was inverted for CCC angles smaller than 100°. Thus, constraining the CCC angle to less than 100° could lead to preferred disrotatory instead of conrotatory ring closure of trimethylene to cyclopropane. The preferred disrotatory ring closure of the trimethylenes arising from the pyrolysis of the pyrazolines of Table III cannot be due to this angle effect since heavy substitution can be expected to increase the CCC angle relative to that of the unsubstituted trimethylene in its equilibrium geometry. Hoffmann's observation of HOMO inversion in trimethylene becomes less significant when configuration interaction is allowed, since whether the S or the A level is higher by 0.5 eV, configuration interaction will strongly mix both S^2 and A^2 configurations. In some further developments, recent calculations indicate that trimethylene can close by an out-of-phase rotatory motion of the two carbon–carbon bonds, as well as an in-phase rotatory motion of the two carbon–carbon bonds,[13b] and these possibilities have to be considered also. The possibility that substituents might influence the mode of ring closure of trimethylene by affecting the dynamic properties of a biradical cannot be dismissed on the basis of these results.

Table VI. Substituent Effects on the Stereochemistry of Trimethylene Ring Closures

Pyrazoline C_3 C_4 C_5	Retention/inversion C_3–C_4	 C_4–C_5	 C_3–C_5	Ref
	1.0			*a*
	1.38			*b*
	98	Infinite	98	*c*
	10.1	32.3	15.7	*c*
	Infinite	3.96	3.96	*c*

[a] D. E. McGreer, N. W. K. Chiu, M. G. Vinje, and K. C. K. Wong, *Can. J. Chem.*, **43**, 1407 (1965). [b] R. J. Crawford and G. L. Erikson, *J. Amer. Chem. Soc.*, **89**, 3907 (1967). [c] D. E. McGreer and J. W. McKinley, *Can. J. Chem.*, **49**, 105 (1971).

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(12) K. Hsu, R. J. Buenker, and S. D. Peyerimhoff, *J. Amer. Chem. Soc.*, **93**, 2117 (1971); R. J. Buenker, S. D. Peyerimhoff, and K. Hsu, *ibid.*, **93**, 5005 (1971).

(13) (a) M. J. S. Dewar and S. Kirschner, *ibid.*, **93**, 4290, 4291, 4292 (1971); (b) P. J. Hay, W. J. Hunt, and W. A. Goodard III, *ibid.*, **94**, 638 (1972); see also the important work of Salem on trimethylene in particular and on diradicals in general: L. Salem, *Bull. Soc. Chim. Fr.*, 3161 (1970); Y. Jean and L. Salem, *Chem. Commun.*, 382 (1971); L. Salem and C. Rowland, *Angew. Chem., Int. Ed. Engl.*, **11**, 92 (1972).

(14) W. Th. A. M. van der Lugt and L. J. Oosterhoff, *J. Amer. Chem. Soc.*, **91**, 6042 (1969).

(15) R. Hoffmann, *ibid.*, **90**, 1475 (1968).

We hope that the analysis offered in the paper will stimulate research on the effects of substituents on the stereochemistry of electrocyclic reactions. In conclusion, we would like to signal out the people who have expressed ideas related to the ideas contained in this paper. Most notably, Baldwin, *et al.*,[16] have provided a classic experimental demonstration of the importance of configuration interaction in lowering the barrier to isomerization of various olefins. These workers observed a linear relation between the activation energies of various thermal isomerizations and the ultraviolet transitions of the reactants.[17]

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(16) J. E. Baldwin and A. H. Andrist, *J. Amer. Chem. Soc.*, **93**, 3289 (1971).

(17) Subsequent to submission of these papers, Breslow and coworkers reported some intriguing substituent effects on electrocyclic reactions which support the conclusions reached in this work: R. Breslow, J. Napierski, and A. H. Schmidt, *ibid.*, **94**, 5906 (1972).

Configuration Interaction and Organic Reactivity. III. Sigmatropic Reactions and Ionic Rearrangements

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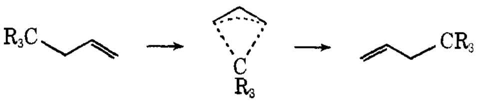
Abstract: The effect of configuration interaction on the stereoselectivity of sigmatropic reactions is examined by a simple molecular orbital approach. It is shown that configuration interaction can reverse the stereoselectivity of 1,3 sigmatropic shifts when the migration framework and the migrating group have widely different polarities. On the other hand, configuration interaction cannot reverse the stereoselectivity of 1,5 sigmatropic shifts. It is also shown that configuration interaction can reverse the stereoselectivity of certain 1,4 cationic and 1,2 anionic rearrangements but not that of 1,2 cationic and 1,4 anionic rearrangements. Experimental evidence relating to these predictions is discussed.

Configuration interaction is important in determining the stereoselectivity of cycloaddition and ring-closure reactions.[2] These ideas are now extended to sigmatropic reactions. Unfortunately, in these cases correlation diagrams cannot be formally constructed. Accordingly, we shall use a simple MO approach in order to gain insights about the effect of substituents on the stereoselectivity of sigmatropic shifts and, in particular, inquire whether configuration interaction can again be important in determining the stereoselectivity of such reactions.

1,3 Sigmatropic Shifts. The transition state of a 1,3 sigmatropic shift involves the interaction between the migrating group, which can be formally represented by the radical $R_3C\cdot$, and the migration framework, which can be formally represented by the allyl radical.



One can distinguish three types of substitution patterns and these are shown in Table I. We shall now examine in detail the stereoselectivity of the 1,3 carbon shift in each of the three cases.

Case I is a typical AX pericyclic process where the donor partner is the migrating group and the acceptor partner is the migration framework. In such a case, the migrating group is characterized by a low ionization potential and the migration framework is characterized by a high ionization potential. One can conveniently derive the MO's of the transition state complex which involves inversion in the migrating center and the MO's of the transition state complex which involves retention in the migrating center from interaction diagrams.[3] These are shown in Figure 1. The conclusions drawn from such interaction diagrams are straightforward and are stated below.

Table I. Types of Sigmatropic Migrations

Case	Designation	Substituents on migration framework[a]	Substituents on migrating group[a]
I	AX	Electron acceptor	Electron donor
IIa	AD	None	Simple alkyls
IIb	AD	Electron acceptor	Electron acceptor
IIc	AD	Electron donor	Electron donor
III	AX	Electron donor	Electron acceptor

[a] Parent migration framework in the case of 1,3 shifts is the allyl radical and in the case of 1,5 shifts is the 1,3-pentadienyl radical. Parent migrating group is in both cases the methyl group.

(1) Migration by inversion will be a concerted process since the lowest state configuration of the inversion transition state complex involves placing two electrons in an NBMO and two electrons in a BMO of the transition state complex. Thus, there is bonding along the union sites and the transition state is pericyclic in character.

(2) Migration by retention will involve an ion pair since the lowest state configuration of the retention transition state complex involves placing four electrons in two NBMO's of the transition state complex. The

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(2) N. D. Epiotis, *J. Amer. Chem. Soc.*, **95**, 1191, 1200 (1973).

(3) Interaction diagrams are constructed as indicated before and the MO's of the transition state complexes are calculated from perturbation theory.