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Orbital Symmetry Control of Chemical Reactions

The tendency to maintain bonding governs the complex motions of molecules in the course of reaction.

Roald Hoffmann and R. B. Woodward

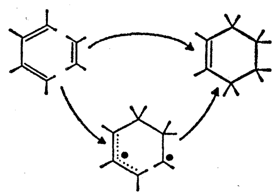
Molecules are complicated three-dimensional assemblages of nuclei and electrons, in which the atomic substructure is to a great degree preserved. It is three-dimensional awareness of the structure of molecules which most distinguishes modern chemists from their predecessors of 50 years ago. The phenomenal advances in x-ray crystallography, electron diffraction, microwave and magnetic resonance spectroscopy and other methods of structure determination, the general availability of molecular models, the willingness of publishers and editors to set in type two-dimensional representations of three-dimensional structures—all of these factors have created a revolution in our image of what molecules really look like and what we can conceive of them doing or not doing in the course of a chemical reaction. The perfection of the ability to think in three dimensions has, however, had one deleterious consequence.

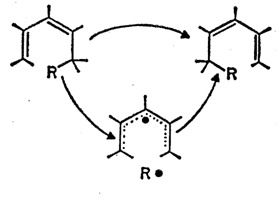
As the molecule as a three-dimensional graph became more easily visualized in the minds of researchers, there came the inevitable side effect of attributing to the model too much rigidity and of thinking of its transformations exclusively in terms of the mechanical billiard-ball experiences of the exterior world. That is, in spite of what was known about molecules rotating and vibrating and about the spatial delocalization of electrons, all these motions being controlled by quantum mechanics, chemists returned to the mental equivalent of a ball-and-stick model in analyzing chemical transformations. Thus in the construction of potential energy surfaces for chemical reactions one easily fell into the habit of assuming least motion of nuclei along the reaction path. Presumably the electrons would readjust to the bulk nuclear motions.

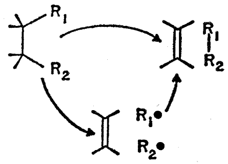
In the last few years, with the aid of some qualitative but extremely powerful quantum mechanical arguments, it has become clear that the primary factor which determines the reaction path of any chemical reaction is the necessity of maintaining maximum bonding throughout the reaction (*1*). We have in effect a least-motion principle for electrons and not for nuclei. Some remarkably specific chemical reactions have been explained, and some striking verifiable predictions have been made and confirmed. It is now clear that in the course of a chemical reaction the nuclei of the reaction components may undergo some extremely complicated motions in order to provide low-energy electronic paths.

General Theoretical Development

The question of concertedness arises whenever more than one bond is broken or formed in the course of a chemical reaction. For each of the three cases illustrated below a concerted pathway is contrasted with one proceeding through diradical intermediates.







The nonconcerted reaction leads from reactants *R* to products *P* through an intermediate molecule or set of molecules, usually comparatively unstable, with a net diradical structure which we will call *D*. We can follow the energy levels of all components through this nonconcerted reaction. The reactants *R* as well as the products *P* are normal ground-state singlet molecules, with a sizable energy gap separating a band of doubly occupied molecular orbitals from a band of antibonding unoccupied orbitals. The diradical intermediate *D* is characterized by one less bonding orbital and one less antibonding orbital than *R* or *P*. Instead, *D* possesses two

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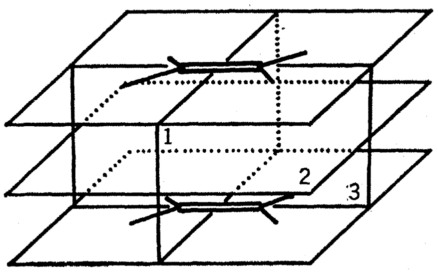
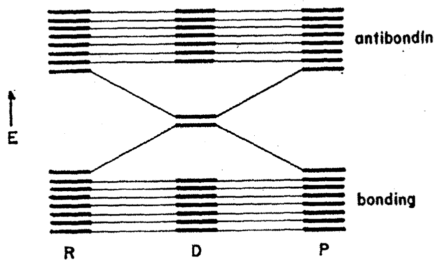


Fig. 1. The high-symmetry approach of two ethylene molecules. Three mirror planes of symmetry are shown.

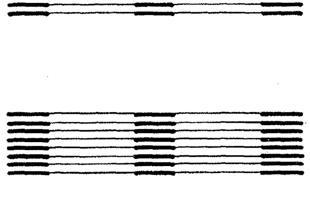
approximately nonbonding orbitals (see *2*).

As the reaction progresses from *R* through *D* to *P*, the individual energy levels move approximately as follows:



It is obvious that in the absence of special circumstances which stabilize the diradical intermediate or destabilize the reactants or products, or both, this will be a high-energy process. The high activation energy is created by the destabilization of a bonding orbital of *P* carrying two electrons to a relatively high-energy nonbonding position in *D*. It will normally be the highest occupied molecular orbital of *P*, its weakest bond, which will become nonbonding in the nonconcerted process.

In our work we realized that the distinguishing characteristic of a concerted, low-activation energy process is that in the course of the reaction the levels move not as illustrated above, but rather in such a way as to avoid the high-energy diradical situation. If there is a direct pathway leading from *R* to *P* in which all new bonds are formed in a tightly time-correlated, if not synchronous, manner, then the energy levels will be transformed as follows:

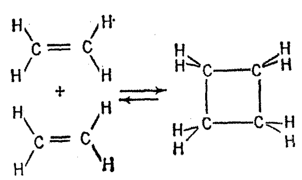


The significant feature of the concerted reaction is then that in the course of reaction, and in particular at its energetic high point, the transition state, all levels derived from bonding levels of reactants remain bonding and all antibonding levels remain antibonding.

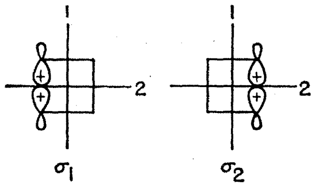
To distinguish the two situations we have utilized a variety of qualitative but powerful molecular orbital arguments: simple scrutiny of the bonding properties of the decisive highest occupied molecular orbital, the construction of correlation diagrams, and the examination of interaction diagrams for the transition state (*1*). The same results could be achieved with detailed calculations of the potential surfaces for these reactions. However, the simple qualitative arguments are based on the most fundamental properties of molecules, such as bonding, overlap, symmetry, and nodal properties. If correctly formulated, such arguments, although qualitative, are much stronger than any approximate numerical calculation and in fact provide a gauge by which any future theoretical treatment must be measured.

The 2 + 2 Cycloaddition

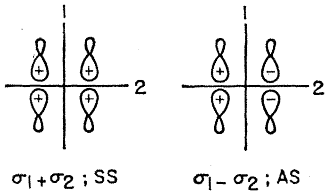
Let us first examine the dimerization of ethylene to cyclobutane, or the reverse reaction:



The least-motion approach is highly symmetric (Fig. 1). This approach is characterized by D_{2h} symmetry, and it is a simple matter to construct a level correlation diagram (*3*) relating the orbitals of the reactants, two ethylene molecules, to the product, cyclobutane. Of the several symmetry elements maintained in the approach geometry, it will suffice to classify levels with respect to their being symmetric (*S*) or antisymmetric (*A*) under reflection in the mirror planes 1 and 2. The semilocalized π levels of the individual ethylene molecules or the σ bonds of the cyclobutane molecule are not proper molecular orbitals of the complex. In order that the orbitals satisfy the property of being symmetric or antisymmetric with respect to every symmetry operation under which the molecule is invariant, proper symmetry-adapted combinations must be formed. Application of the procedures of group theory (*4*) yields such combinations automatically, and in most cases the simple process of forming all possible independent sums and differences of the component orbitals will suffice. Thus the isolated σ bonding orbitals of the cyclobutane σ_1 and σ_2



while not being either symmetric or antisymmetric with respect to reflection in plane 2, may be combined into the symmetry-adapted $\sigma_1 + \sigma_2$ and $\sigma_1 - \sigma_2$.



The σ^* orbitals of cyclobutane and the π and π^* orbitals of the ethylene molecule are analogously combined (*5*).

The level correlation diagram of Fig. 2 may then be constructed by connecting to each other levels of the same symmetry. The most obvious and striking feature of this diagram is the correlation of a bonding reactant level with an antibonding product level and the correlation of an antibonding reactant level with a bonding product level. This correlation results in two high-energy nonbonding orbitals in the transition state for the reaction, a situation plainly analogous to our general considerations for a nonconcerted process.

The matter may be further illuminated by inspection of the corresponding state diagram (*6*) for the reaction (Fig. 3). The ground-state electron configuration of two ethylene molecules correlates with a very high-energy, doubly excited state of a cyclobutane molecule; conversely, the ground state of cyclobutane correlates with a doubly excited state of two ethylene molecules. Electron interaction will prevent the resulting crossing (*7*) and force a correlation of ground state with ground state. But in the actual physical situation, the reaction still must pay the price in activation energy for the intended but avoided crossing. An order-of-magnitude estimate of the symmetry-imposed energy barrier to the concerted face-to-face combination of two ethylene molecules may be made by considering the energy required to raise two bonding electrons in the occupied bonding level to the nonbonding level —perhaps 5 electron volts or about 115 kilocalorie/mole. No symmetry-imposed barrier intervenes in the excited-state complex of two ethylene molecules. The dimerization of two ethylene molecules in the least-motion transition state is clearly a ground state forbidden and excited state allowed process.

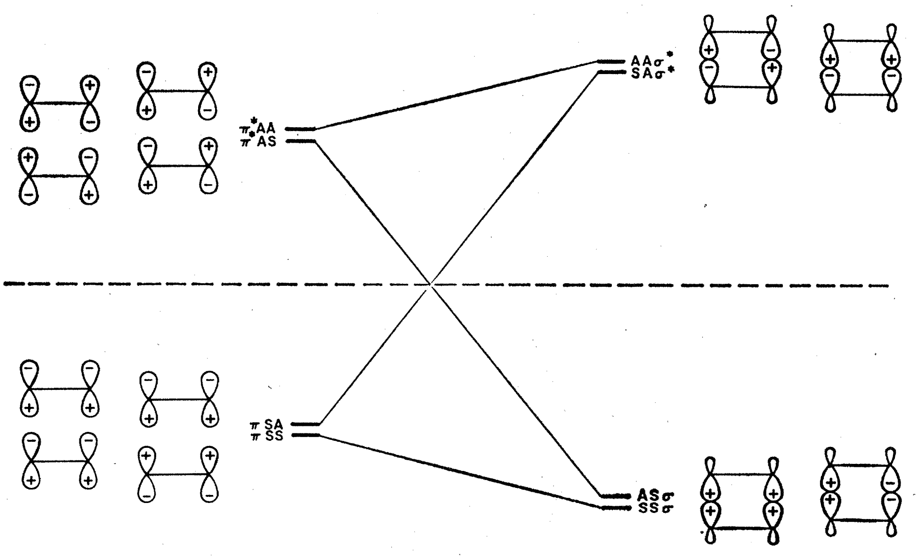
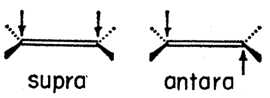


Fig. 2. Level correlation diagram for the high-symmetry dimerization of ethylene. Only those levels which are significantly affected by the reaction, that is, the ethylene π and π^* levels, and the newly formed σ and σ^* levels of the cyclobutane, are included. The dashed horizontal line is an approximate nonbonding energy. Planes 1 and 2 of Fig. 1 are used for classifying the symmetry properties of the levels.

There exists, however, a reaction pathway by which two ethylene molecules may form cyclobutane while preserving the bonding character of all occupied energy levels. It occurs through a nonleast-motion process in which addition to one ethylene is on the same side or *suprafacial*, whereas on the other ethylene the addition occurs on opposite sides, which we term an *antarafacial* process. The choice between *cis, syn*, or *suprafacial* and *trans, anti* or *antarafacial* modes of addition to a double bond has long been a legitimate primary concern of physical organic chemists studying additions of species such as hydrogen halides to olefins (*8*). The two addition modes are operationally distinguishable when the substrate is either a cyclic olefin or an ethylene sufficiently labeled to exhibit geometrical isomerism.



A priori we may ask the mode of addition for each component in the reaction. We use a notation in which the dynamic modes *suprafacial* or *antarafacial* are designated by the use of subscript letters *s* or *a* shown after the number of electrons involved in each cycloaddition component. Thus the ethylene dimerization which we have shown to be thermally forbidden is $2_s + 2_s$, and the allowed process now being described is $2_s + 2_a$. The two pathways are operationally distinguishable through their products if the reactants are labeled to exhibit geometrical isomerism (see Fig. 4). The electronic allowedness of the $2_s + 2_a$ cycloaddition may be revealed by the correlation diagram for the process, if we use the twofold rotation axis which is preserved. By comparison with the least-motion $2_s + 2_s$ transition state, the $2_s + 2_a$ pathway is encumbered by the much less favorable steric environment of the inner hydrogens of the 2_a component, and by the double bond torsion which must accompany bond formation. These obvious difficulties prevent the ethylene dimerization or its reversion from being facile processes. One can transform the same difficulties, however, into positive advantages by providing molecules in which the offending hydrogens are removed or in which the requisite torsion is built in. It is only for such species that the $2_s + 2_a$ reaction has so far been experimentally observed. Each of the four cases shown below is com-

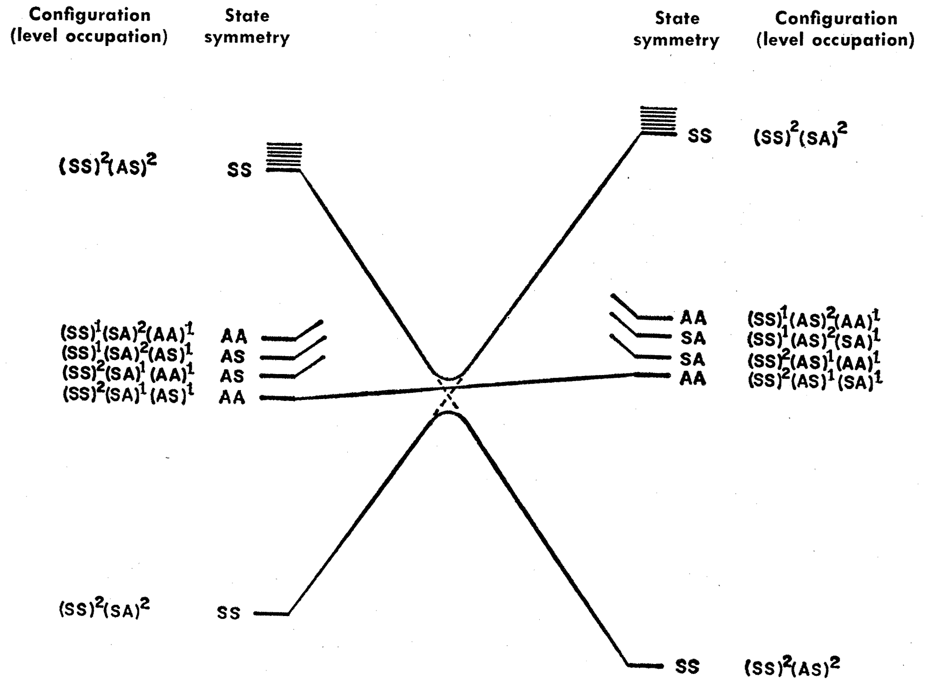
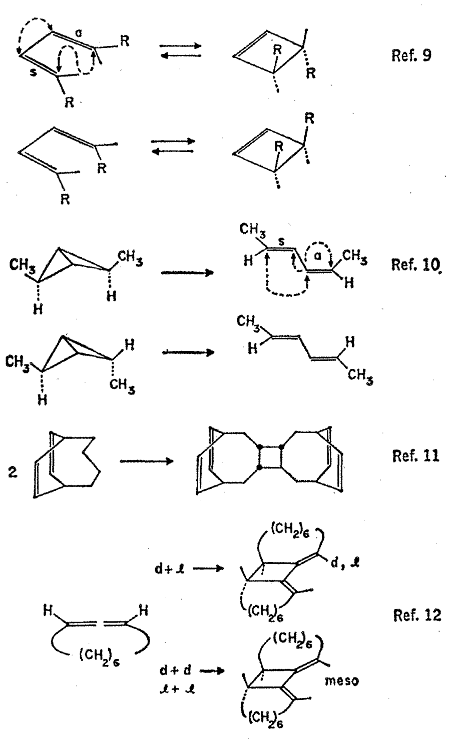


Fig. 3. State correlation diagram for the dimerization of ethylene. The symmetry of the states is obtained by multiplying the symmetry labels for each electron, according to the rules (*3, 4*)

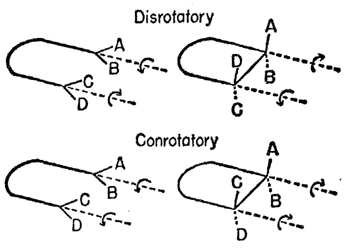
$$S \times S \rightarrow S \leftarrow A \times A$$
$$S \times A \rightarrow A \leftarrow A \times S$$

Only singlet excited states are shown, and at this level of sophistication they should be regarded as degenerate at either extreme of the diagram.

pletely stereospecific. In each case other stereochemical outcomes were a priori possible and would in fact have been consistent with nonconcerted processes.

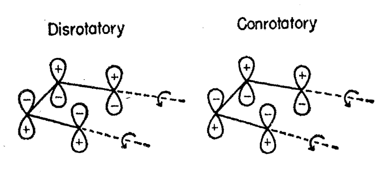


The first reaction in the above scheme is the well-known electrocyclic interconversion of a butadiene and a cyclobutene. The ring closure could have been imagined to proceed in either a conrotatory or disrotatory sense (*1*)



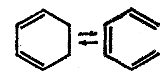
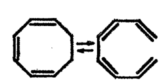
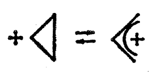
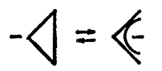
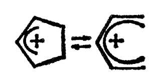
or in some nonconcerted combination of both. In a specific case an average molecule carries out *at least* 10^6, and probably several orders of magnitude more, faultlessly conrotatory motions before a disrotatory mistake is made (*13*).

The original simple argument we used for deciding that the conrotatory motion is preferred remains pertinent (*1*). Consider the effect of the two motions on the highest occupied molecular orbital of butadiene (*14*).

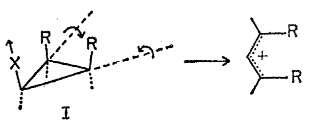


The conrotatory motions provide positive overlap, and thus bonding and attraction. The disrotatory motions force a plus lobe of one terminus on the minus lobe of the other. This is a destabilizing, repulsive interaction which creates the nonbonding situation characteristic of a nonconcerted process. Note the essential quantum mechanical nature of the argument in its reliance on the relative phase of the wave function.

The same stereochemical question that arises in the butadiene-cyclobutene interconversion may be asked of other valence isomerizations. The analysis is just as simple, and our predictions have been confirmed in every case studied.

	Δ	hν	reference
	dis	con	15
	con	dis	16
	dis	con	17
	con	dis	18
	con	dis	19

A most interesting subsidiary question in connection with the electrocyclic opening of a cyclopropyl cation to an allyl cation was first posed to us by C. H. De Puy: If we assume that the departure of a leaving group from a cyclopropane ring, and the bond-breaking electrocyclic reaction to give an allyl cation, are concerted, could there be a difference between the two a priori possible disrotatory modes, defined in relation to the position of the leaving group? Extended Hückel calculations (*20*) provided the initial answer, which may be summarized by saying that the substituents on the same side of the three-membered rings as the leaving group rotate toward one another, whereas those on the other side rotate apart.



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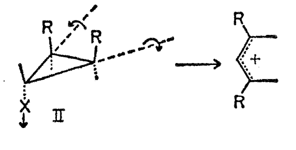
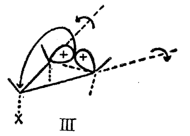


II

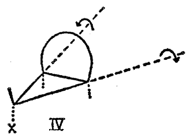
The result may be understood in qualitative terms when it is realized that as the bond between C-2 and C-3 is broken by disrotatory outward rotation (see III), the electron density



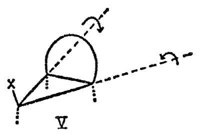
III

of that bond, which originally was more or less in the plane of the cyclopropane ring, shifts above the plane. It is then available for backside displacement of the leaving group—in other words, the reaction is a normal nucleophilic substitution displacement of the group X by the electrons of the backbone σ bond of the cyclopropane ring.

Several corollaries of these conclusions follow. If R is some bulky group as in compounds I or II, then we should expect for steric reasons a faster solvolysis for compound II. On the other hand, when *cis* positions are linked by a short methylene chain we should expect the opening of a compound such as structure IV with the leaving group *anti* to the ring to be severely disfavored, since the resulting rotation would lead to a *trans-trans* allyl cation in a small ring. We should expect a facile opening only for a *syn* leaving group, as in structure V.

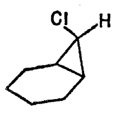


IV

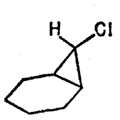


V

These predictions have been found to be reliable (*17*). For example, whereas compound VI undergoes solvolysis readily at 125°C, its epimer VII



VI

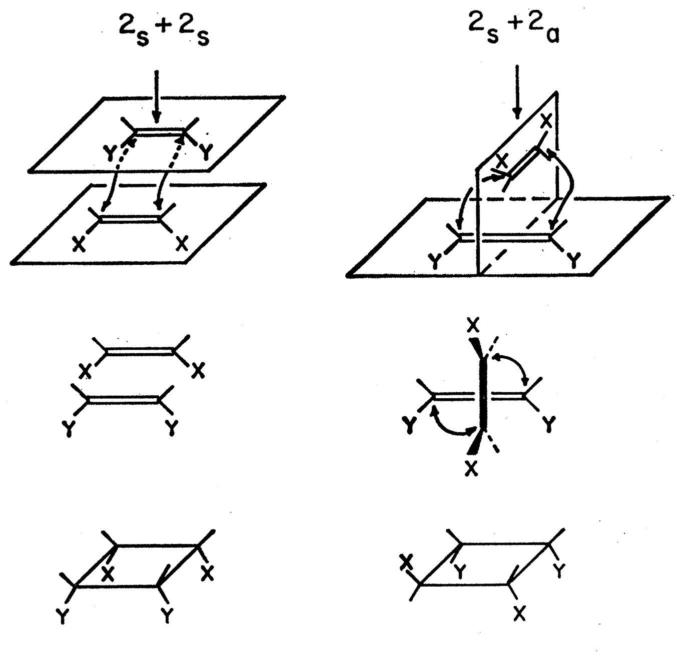


VII

is recovered unchanged after prolonged treatment with acid at 210°C [see references in (*17, 21*)]. In the electrocyclic reactions of cyclopropyl cations, one thus finds straightforward examples of the subservience of steric control to primary electronic effects.

Sigmatropic Shifts

Consider another possible concerted process, a degenerate 1,3 shift of a



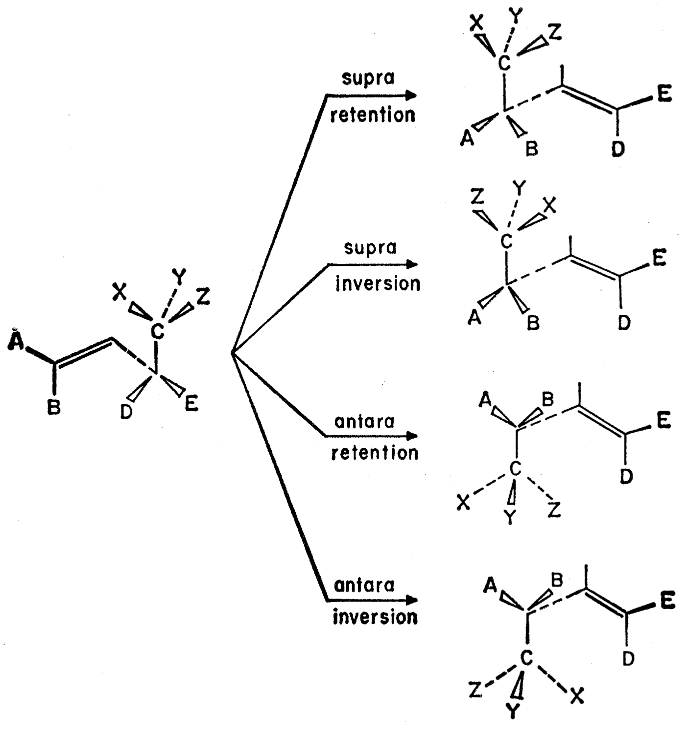
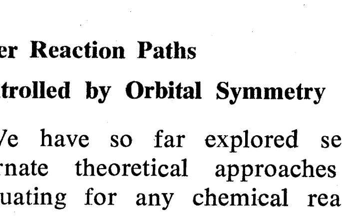


Fig. 4 (left). Approach geometrics for $2_s + 2_s$ and $2_s + 2_a$ cycloadditions. The ethylenes are labeled originally with *cis* substituents *X* and *Y*. The middle illustration shows an approximate view of the reactants as they would appear if viewed along the arrow direction shown in the top part. The bottom sections show the stereochemical consequences of the cycloaddition. Fig. 5 (right). Four possible stereochemical outcomes of a 1,3 sigmatropic shift. Carbon atom *C* can migrate to the top (suprafacial) or bottom (antarafacial) of C-1 and in the process may undergo retention or inversion. The four possibilities give rise to distinct products.

group *R* in a propylene. The topological questions which may be operationally asked of this process are whether the shift is *suprafacial* (to the top of C-1) or *antarafacial* (to the bottom of C-1) and whether it occurs with retention or inversion at the migrating group *R*. The four possibilities are illustrated in Fig. 5.

The least-motion transition state is clearly the one in which the migration is *suprafacial* with retention. Let us examine whether this process is allowed. Since symmetry elements are absent in reactants or products, we cannot construct an informative correlation diagram for the reaction. We can, however, utilize the symmetry of the transition state to construct an interaction diagram (*22*). In the transition state we may describe the system as a three-center bond (*23*) involving the terminal carbons and the σ orbital of the migrating group, and the radical 2*p* orbital left behind. The interaction of these two systems is shown in Fig. 6.

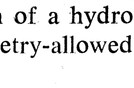
The nonbonding orbital of the three-center bond does not possess the correct symmetry to interact with the remaining *p* orbital. There arises a nonbonding situation in the transition state characteristic of a forbidden reaction. Construction of similar interaction diagrams or the detailed following through of all orbitals for the stereochemical alternatives predicts that the allowed processes are a *suprafacial* shift with inversion and an *antarafacial* shift with retention (*1*). The steric constraints on these transition states are formidable, and yet a clear example of the first process has been realized in the work of Berson (*24*).



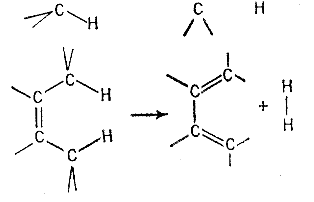
Other Reaction Paths Controlled by Orbital Symmetry

We have so far explored several alternate theoretical approaches for evaluating for any chemical reaction the extent of bonding in the transition state. Still other theoretical analyses are feasible (*25*). In the vast majority of cases simple arguments suffice, and detailed computations are not required. We will now mention briefly some further examples of the type of conclusion we are able to draw, focusing on transition states where nuclear least-motion is most likely to be misleading.

1) The square transition state for the hydrogen exchange reaction,



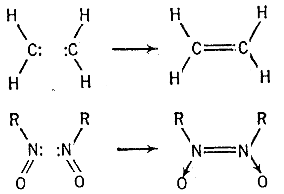
long accepted as the only reasonable transition state for this very simple reaction, should lie at a very high energy (*26*). This has been recently supported by the most accurate calculations on this potential energy surface (*27*). Similarly the vicinal 1,2 elimination of a hydrogen molecule is not a symmetry-allowed process, whereas



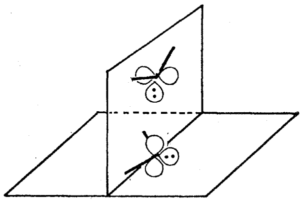
the corresponding 1,4 elimination should be. Some experimental evidence exists to support these conclusions (*28*).

It might be remarked here that our preference for a detailed analysis of reasonably complicated (in terms of atoms) reactions, such as 1,3 migrations or 2 + 2 cycloadditions, is not an irrational choice nor one devoid of conclusions of value to those studying much smaller systems. A balanced evaluation of the tools available to the chemical kineticist indicates that, with the current ease of isotopic labeling and some courage in synthesis, more information can be experimentally obtained concerning the potential surfaces for the reactions of medium-sized molecules (5 to 20 atoms) than for their smaller counterparts.

2) Methylenes dimerize with very little activation energy (*29*), and nitroso compounds do so only slightly less reluctantly (*30*).

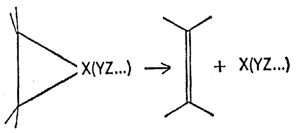


The simplest approach of two planar molecules to form a planar product would appear to be one with both molecules in the same plane, as implied by the above structures. A correlation diagram readily shows that this pathway is a high-energy one. Detailed calculations favor an approach with the two reactants in perpendicular planes, with a lone pair of one molecule impinging initially on an unoccupied nonbonding or low-lying antibonding π orbital of the other (*31*), as shown below for the methylene case.



Eventually bending occurs, leading to the planar product.

3) Three-membered rings are known to readily expel small stable or unstable fragments.



The fragments expelled may be carbon monoxide (*32*), nitrogen (*33*), sulfur dioxide (*34*), nitrous oxide (*35*), and the like. The microscopic reverse of one such process is observed in the well-known addition of singlet methylene (*36*) or of sulfur atoms (*37*) to ethylene. These processes are often stereospecific, and many are suspected of being concerted. The least-motion process is illustrated in Fig. 7. Detailed examination of the orbitals or the construction of a correlation diagram reveal immediately that this "linear" departure or attack is a forbidden reaction. The symmetry-allowed pathway is a "nonlinear" departure (see also Fig. 7) in which the plane containing the departing group shifts from being perpendicular to the ethylene plane to being parallel. The reaction coordinate is best described then not as a pure stretching motion but as a combination of stretching with bending or wagging (*38*). The establishment of a nonleast-motion transition state which leaves no stereochemical traces poses to the experimentalist a most fascinating challenge.

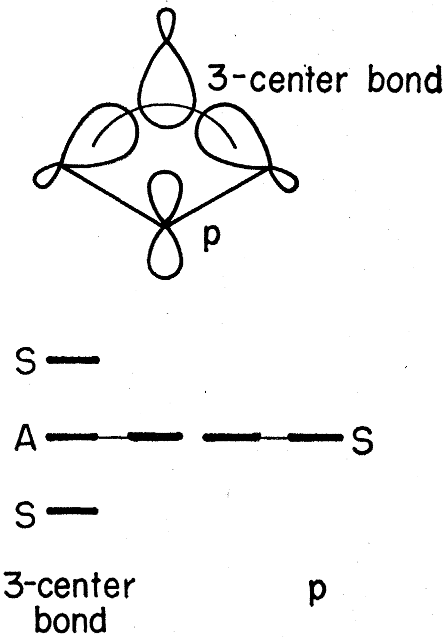


Fig. 6. The top of the figure shows the three-center bond and the remaining *p* orbital. The propylene system is viewed 180° from the position in Fig. 5. At bottom the orbitals are classified with respect to their symmetry properties on reflection in the vertical mirror plane. The allyl orbitals alternate in symmetry (*14*), and the lone *p* orbital lies in the mirror plane and thus must be symmetric.

Summary

One should not conclude from our work that least-motion transition states are unattainable. They should in fact be observed more often than the nonleast-motion ones. Thus orbital-symmetry control favors the $4_s + 2_s$ cycloaddition, which is the normal Diels-Alder reaction; it makes allowed the 1,5 *suprafacial* shift with retention, and it provides for a linear departure of carbon monoxide, accompanied by disrotation, from a cyclopentenone. The symmetry-allowed nonleast-motion pathways are almost by definition discriminated against by steric factors—they will thus often not manage to be competitive with nonconcerted processes.

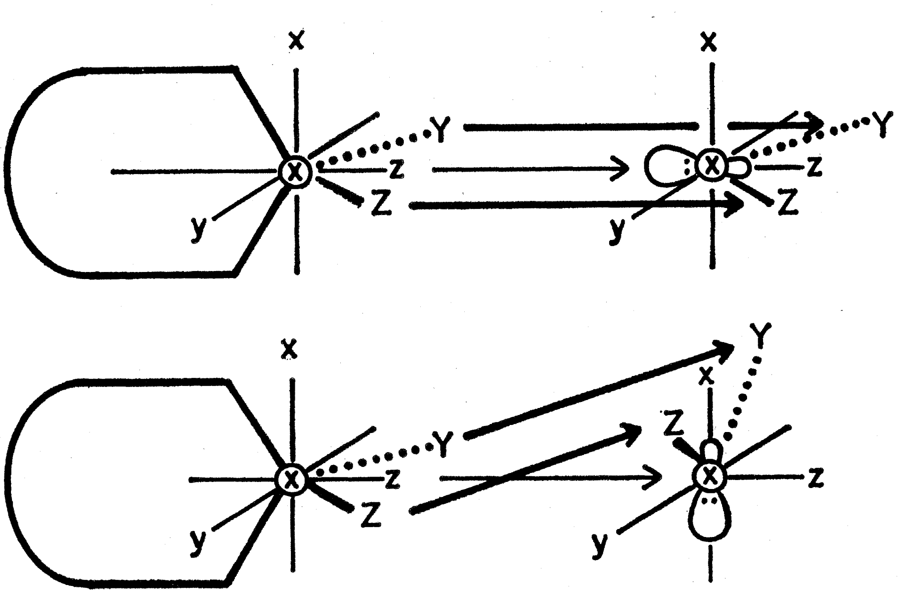


Fig. 7. Linear (top) and nonlinear (bottom) modes of departure of a small molecule *XYZ* from a cyclic species. The ring formed by the carbon atoms and *X* lines in the *xz* plane, and *X* departs approximately along the *z*-axis. In the linear process *Y* and *Z* remain in the *yz* plane as they depart. In the nonlinear process they move up (or down) until they ultimately assume position in a plane parallel to the *xy* plane.

The point of our work is not that least-motion processes are to be ignored. Rather, we urge a refocusing on the primary quantum mechanical electronic nature of all chemical reactions. The preservation of the bonding character of all electrons in a reaction is the primary feature of any chemical change. This tendency to maintain bonding will direct nuclear motions which may or may not be least-motion ones.

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