The Conservation of Orbital Symmetry

By R. B. Woodward[*] and Roald Hoffmann[**]

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In 1965, in a series of preliminary communications [1–3], we laid down some fundamental bases for the theoretical treatment of all concerted reactions. The history of the genesis of these ideas has been described elsewhere [4]. The basic principle enunciated was that reactions occur readily where there is congruence between orbital symmetry characteristics of reactants and products, and only with difficulty when that congruence does not obtain—or to put it more succinctly, orbital symmetry is conserved in concerted reactions. This principle has met with widespread interest; the appli-
When \( \chi_1 \) and \( \chi_2 \) are \( p \) orbitals interacting in a \( \sigma \) manner, and oriented as shown in (2):

\[
\begin{align*}
\chi_1 &= X_1 \times \sigma_1 \\
\chi_2 &= X_2 \times \sigma_2
\end{align*}
\]

Throughout this paper, the planes of wave functions are color-coded: positive = blue, negative = green. When planes orthogonally interact, the orbitals are presented in solid gray.

The bonding combination is again \( \chi_1 \times \chi_2 \) and the antibonding combination \( \chi_1 - \chi_2 \).

\[
\begin{align*}
\chi_1 &= X_1 \times \sigma_1 \\
\chi_2 &= X_2 \times \sigma_2
\end{align*}
\]

It is important to realize, however, that were the basis orbitals initially arbitrarily oriented in some other fashion, such as (3), then, since \( \psi_1 - \psi_2 \), the bonding combination would be \( \chi_1 - \chi_2 \), and the antibonding one \( \chi_1 + \chi_2 \). It should also be kept in mind that multiplying an entire wave function by \(-1\) does not affect its energy. Thus, overlap of minima with maxima lobes is precisely equivalent to plus plus lobes, and \(-\chi_1 - \chi_2\) is the same bonding orbital as \( \chi_1 + \chi_2 \).

\[
\begin{align*}
\chi_1 &= X_1 \times \sigma_1 \\
\chi_2 &= X_2 \times \sigma_2
\end{align*}
\]

(3)

The description of \( \sigma \) bonds in hydrocarbons is simple. Each formal chemical bond engenders a \( \sigma \) and a \( \pi^* \) orbital. The \( C-H \) and \( C-C \) cases are:

\[
\begin{align*}
\sigma_{C-H} &= X_1 \times \sigma_1 \\
\pi^*_{C-C} &= X_1 \times \sigma_1
\end{align*}
\]

The molecular orbitals are represented in our drawings as the overlap of two hybrids of unspecified hybridization. It should be emphasized that this is intended as an artistic mnemonic device: the only essential features of a \( \sigma \) orbital are that it is approximately cylindrically symmetrical around the bond axis, that it concentrates electron density in the region between the nuclei, and that there is no nodal plane between the atoms.

Our simple picture of bonding in, say, cyclohexane, shows four \( C-C \) levels, and eight \( C-H \) \( \sigma \) levels, each with a matching \( \pi^* \) level (4). The carbon 1s orbitals are not considered. Each of the \( \pi \) levels is occupied by two electrons. Spectroscopic studies indicate that the gap between occupied and unoccupied levels must be of the order of 10 electron volts.

The orbitals we have constructed are semi-localized. They are delocalized over only two atoms. Such orbitals are satisfactory for the analysis of symmetry properties of a molecule through the full symmetry of the molecule. For a discussion of physical properties depending on one or two specific molecular orbitals, such as spectra or ionization, it is absolutely necessary to construct these equivalent delocalized orbitals. The mechanism of delocalization will be described in Section 3.

In addition to \( \sigma \) bonds, the molecules of organic chemistry contain delocalized \( \pi \) orbitals. Thus, the electronic structure of ethylene is described as follows: There are four \( C-C \) bond orbitals and a \( C-C \) bond (4). Each of the ethylene orbitals under each of the above operations is precisely opposite. Thus, the orbital is symmetrical (5) with respect to the mirror plane \( m \), and antisymmetrical (6) with respect to the rotation axis \( C_2 \).

The overlap between the two \( 2p \) orbitals is significant in molecules of the allyl system. Figure 2. Their nodal structure should be carefully noted. By virtue of their character as \( \pi \) orbitals, they are all antisymmetric under reflection in the plane of the allyl system. The lowest orbital, doubly occupied in the allyl cation, has no additional nodes. The middle, nonbonding orbital, which is singly occupied in the allyl radical, and doubly occupied in the anion, has a single nodal plane which precludes any contribution of the \( 2p \) orbital of the central carbon atom. The orbital of highest energy has two nodes.

The molecular orbitals of the four-orbital butadiene system are shown in Figure 3 for an \( xx \) arrangement. The electronic structure of polymers is perhaps the most highly developed branch of semi-empirical molecular orbital theory. A very good survey of the field is given in I. J. Siegel, The Molecular Orbital Theory of Conjugated Systems. Benjamin, New York 1969, see also D. Streitweiser, Molecular Orbital Theory for Organic Chemistry. Wiler, New York 1961.
The orbitals alternate in symmetry with increasing energy.
If \( n \) is even, there are \( n/2 \) bonding \( n \) orbitals and \( n/2 \) antibonding. If \( n \) is odd, there are \((n-1)/2\) bonding, \((n+1)/2\) antibonding, and one nonbonding orbital.

A final point of much importance is that no molecular orbital may be at the same time symmetric and antisymmetric with respect to any existing molecular symmetry element. Thus, the orbital \( \psi_0 \) is symmetric under rotation by 180° if atoms 2 and 3 are viewed, but antisymmetric if 1 and 4 are considered; it is not an acceptable molecular orbital of butadiene.

3. Correlation Diagrams

The united atom-separated atom diatomic correlation diagrams first drawn in the early nineteen-thirties by Head and Mulliken have an important place in theoretical chemistry. In constructing such a diagram, one imagined the process of two atoms approaching each other from infinity. The energy levels of the separated atoms were placed in approximate order of energy on one side of the diagram. One then imagined the approach of the atoms through the physically realizable molecular region into the physically impossible process of nuclear coalescence. The energy levels of the resulting united atom were once again known. They were placed on the other side of the diagram. Thus, one proceeded to classify the initial separated and the final united atom orbitals with respect to the symmetry maintained throughout the hypothetical reaction. Levels of like symmetry were connected, passing due attention to the quantum mechanical noncrossing rule—that is, only levels of unlike symmetry are allowed to cross (Figure 4).

In this way, from the relatively well-known level structures of the separated atoms and the unknown atom-valence information was obtained about the level structure of the intermediate region corresponding to the molecule. It was this kind of diagram which provided a rationalization for the existence of the oxygen molecule as a ground-state triplet.

In an exactly analogous manner a correlation diagram may be drawn for a concerted reaction such as cyclodimerization. One side one writes down the approximately known energy levels of the reactants, on the other side those of the product. Assuming a certain geometry of approach one can classify levels on both sides with respect to the symmetry maintained throughout the approach, and then connect levels of like symmetry. Such a molecular correlation diagram yields valuable information about the intermediate region, which represents in this case the transition state for the reaction.

We would like to illustrate in some detail the construction of a molecular correlation diagram. The first example we choose is the maximum-symmetry approach of two ethylene molecules, leading to bicyclobutane (Figure 5). As usual in theoretical discussions, maximum insight into the problem at hand is attained by simplifying the case as much as possible, while maintaining the essential physical features. In this instance we treat in the correlation diagram only four orbitals—the four \( \pi \) orbitals of the two ethylenes. In the course of the reaction these four \( \pi \) orbitals are transformed into four \( \sigma \) orbitals of cyclobutane. We may safely omit the C–H and the C–C bonds of the ethylene skeleton from the correlation diagram because, while they undergo hybridization changes in the course of the reaction, their number, their approximate positions in energy, and in particular their symmetry properties are unchanged.

The first step in the construction of a correlation diagram involves isolating the essential bonds and placing them at their approximate energy levels in reactants and products; the result is shown for the case at hand in Figure 6, in which the dashed horizontal line is the

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Footnotes:

neighboring level — approximately the energy of an electron in a free carbon 2p orbital. We have separated \( \sigma \) and \( \pi^* \) by an energy greater than that between \( \pi \) and \( \pi^* \); although there is little reason to question this assignment, it is important to emphasize that it is in no way essential to the subsequent argument. To assign an order of magnitude to the vertical energy scale we may take the distance between it and \( \pi^* \) as approximately 5 electron volts.  

In the next step the proper molecular orbitals for the reactants and products are written down. A discussion on constructing molecular orbitals for interacting systems is in order at this point. Consider an \( \sigma \)-trans-butadiene. One way to derive the four molecular orbitals of butadiene is to allow all of the four atomic orbitals to interact as illustrated at left in (9).

Yet another way is to view butadiene as arising from the interaction of two semi-localized double bonds. Consider the bonding \( \pi \) orbitals of the two ethylenes. While \( \pi_1 \) and \( \pi_2 \) are entirely satisfactory for a description of the isolated double bonds, they are not the proper combinations to use as molecular orbitals for butadiene. Molecular orbitals must be symmetric or antisymmetric with respect to any molecular symmetry element which may be present. In the case at hand the crucial symmetry operation is a 180° rotation around the two-fold axis. The obvious combinations to use, and ones which do satisfy the symmetry conditions, are \( \pi_1 + \pi_2 \) and \( \pi_1 - \pi_2 \). These, of course, turn out to be topologically identical with the two lowest-energy butadiene orbitals which were constructed by considering direct interaction of all four atomic orbitals.  

We are now prepared to treat the analogous problem of the molecular orbitals of two ethylenes approaching each other. Drawing orbital cross-sections in plane 3 (c.f. Figure 5), diagram (11) represents localized \( \pi \) bonds of the two ethylenes. These are not the proper combinations to choose for a discussion of the orbitals of the complex of two ethylenes; they are not symmetric or antisymmetric under reflection in plane 2. Again the obvious combinations are \( \pi_1 + \pi_2 \) and \( \pi_1 - \pi_2 \).  

The first of these is symmetric with respect to reflection in both planes 1 and 2 (abbreviated as \( S_S \) or simply \( SS \)); the second is symmetric under reflection in plane 1, and antisymmetric under reflection in plane 2 (\( S_A \) or \( SA \)) [9]. Both orbitals, of course, are symmetric with respect to reflection in plane 3, and this trivial information need not be explicitly specified. At large separations between the ethylenes, \( \pi_1 + \pi_2 \) and \( \pi_1 - \pi_2 \) will be degenerate, but at small separations \( \pi_1 + \pi_2 \) will be at lower energy than \( \pi_1 - \pi_2 \); since the former has fewer nodes. Similar combinations of antibonding molecular orbitals for the complex are shown in (13).  

One must next analyze the situation in cyclobutane in an entirely analogous way. Consider the localized \( \sigma \) bonds (14). Again these do not satisfy all the symmetry operations of the cyclobutane molecule, and one must take the two combinations \( \sigma_1 + \sigma_2 \) (15); a similar procedure must be followed for the antibonding \( \sigma^* \) orbitals (16).

We are now equipped to examine the correlation of the orbitals of reactants with those of the product (Figure 7). The direction in which the various levels will move may be obtained without detailed calculations.
occupying it lie in the region between and are shared by the nuclei. σ is antibonding at higher energy because the presence of a node between the nuclei isolates electrons populating the orbital in the region of the individual terminal nuclei. There is another aspect of bonding or antibonding displayed in this schematic diagram: electrons placed in a bonding orbital bring the nuclei closer together (that is, for σ, SE/GR=0), while electrons put into an antibonding orbital push the nuclei apart (that is, for σ, SE/GR=0).

Returning to the ethylene correlation diagram (Figure 7), we find that the lowest SS level of two ethylenes is bonding in the region of approach of the two molecules to each other and thus will be stabilized by interaction. The SA level has a node, and consequently is antibonding in the region of approach. At large distances the interaction is inessential, but as the distance between the reacting molecules diminishes, this orbital is destabilized and moves to higher energy. Similarly, the antibonding σ* AS orbital becomes bonding in the region of approach. It will thus be stabilized as the reaction proceeds, while the σ* AA orbital will be destabilized.

On the cyclobutane side both the σ levels, SS and AS, are bonding in the region where the cyclobutane is being pulled apart. Thus, they resist the motion—that is, they are destabilized along the reaction coordinate. On the other hand, the σ* levels SA and AA are antibonding along the reaction coordinate and thus move to lower energy as the cyclobutane is pulled apart.

That these qualitative conclusions are correct may be seen from a completed correlation diagram in which levels of like symmetry are connected (Figure 9). The most obvious and striking feature of this diagram is the correlation of a bonding reactant level with an antibonding product level, and vice versa.

We now approach a central tenant of our treatment of concerted reactions. Clearly, if orbital symmetry is to be conserved, two ground-state ethylene molecules cannot combine in a concerted reaction to give ground-state cyclobutane—nor can cyclobutane be decomposed in a concerted fashion to two ethylene molecules, through a transition state having the geometry assumed here. To put the matter in other words, there is a very large symmetry-imposed barrier to the reaction under discussion, in either direction. By the same token, there is no such symmetry-imposed barrier to the reaction of one molecule of ethylene with another, one of whose electrons has been promoted, say by photochemical excitation, to the lowest antibonding orbital. For these reasons we designate reactions of the first type symmetry-forbidden, and those of the second symmetry-allowed.

The matter may be further illuminated by inspection of the corresponding state diagram for the reaction (Figure 10). The ground state electron configuration of two ethylene molecules correlates with a very high-energy doubly excited state of cyclobutane; conversely the ground state of cyclobutane correlates with a doubly excited state of two ethylenes. Electron interaction 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 non-bonding level—perhaps 5 eV or about 115 kcal/mole.

The lowest excited state of two ethylenes, the configuration (SS)(SA)(AA)(AS), correlates directly with the first excited state of cyclobutane. Consequently, there is no symmetry-imposed barrier to this transformation. This represents the course which is followed in many photochemical transformations. However, it should be emphasized that there are ambiguities in excited state reactions which do not exist in their simpler thermal counterparts. Thus, it may happen that the chemically reactive excited state is not that reached on initial excitation, in particular, single-triplet splittings for different excited states vary so widely that the symmetries of the lowest singlet and lowest triplet states may differ. Further, radiationless decay may be inefficient so that the chemical changes subsequent to irradiation may be of a vibrationally excited ground state. Finally, the formation of a transition state for a given concerted reaction may be competitive with relaxation of the excited state component to an equilibrium geometry which renders the reaction geometrically impossible. It should be emphasized that none of these perturbations in any way vitiate the consequences of orbital symmetry.
control. The principle of conservation of orbital symmetry remains applicable, provided that the chemically reactive excited state is isolated. Furthermore, the fact that the product state which correlates directly with the reactant state may lie higher in energy than the latter constitutes no special problem in orbital symmetry terms — though admittedly there is still much to be learned about the detailed physical nature of the processes accompanying the necessary energy cascade from electronically excited to ground states in such instances.

Many correlation diagrams differ sharply from that for the ethylene + ethylene reaction. Consider for example the prototype Diels-Alder reaction — the [4+2] cycloaddition of butadiene to ethylene. The most reasonable symmetric approach is characterized by a single plane of symmetry bisecting the two components (Figure 12). The form of the four butadiene and two ethylene orbitals is self-evident. We have placed the ethylene π level between the two bonding diene orbitals, but the ordering is not consequ-

![Figure 11: Symmetric approach of butadiene and ethylene in the Diels-Alder reaction.](image)

![Figure 12: Correlation diagram for the Diels-Alder reaction of butadiene with ethylene.](image)

On the product cyclohexene side note that one must construct delocalized π bond combinations just as was done for cyclobutene.

The difference between the correlation diagram and that for the combination of two molecules of ethylene is striking. In this case every bonding level of reactants correlates with a bonding product level; there is no correlation which crosses the large energy gap between bonding and antibonding levels.

![Figure 13: Electrostatic map diagram for the Diels-Alder reaction of butadiene with ethylene.](image)

As before one may construct a state diagram (Figure 13). The ground state levels correlate directly, and the diagram implies that there is no activation energy at all for this thermal symmetry-allowed process. And indeed, there is no symmetry-imposed barrier, but of course there is an activation energy — experimentally found to be approximately 20 kJ/mol — which arises from factors not simply related to orbital symmetry conservation; among them are energy changes accompanying rehy-

![Figure 14: Configuration diagram for the Diels-Alder reaction of butadiene with ethylene.](image)

As a rule here: If two levels of unlike energy interact, that of the lower energy will mix into itself some of the higher-energy wave function in a bonding way, but the higher level will mix into itself some of the lower one in an antibonding way. If these two levels interact, their mixing can be analyzed as a superposition of such pair-wise interactions. The application of this rule is illustrated here for the formation of a C-H bond from a carbon sp hybrid and a hydrogen 2p orbital (17). In the case of butadiene — ethylene we find that the olefin π level mixes into itself (1) in an antibonding way and (2) in a bonding way (18). The diene HOMOs cancel at C-1 and C-4 of the butadiene.
sity, but reinforce at C-2 and C-3. Thus, in the transition state this orbital is essentially half in the one and half in the other of the reacting molecules.

If one considers further cases of the general cycloaddition reaction of an \( n \) \( \pi \)-electron system with an \( m \) \( \pi \)-electron system to form two new \( \pi \) bonds, while maintaining a plane of symmetry, it becomes evident that there are only two types of correlation diagrams:

a) those similar to that of the Diels-Alder reaction, with no correlation of bonding and antibonding levels, and characterized as symmetry-forbidden for ground states and symmetry-allowed for excited states;

b) those similar to that for the ethylenè - ethylene combination, which display bonding-antibonding correlations, and are consequently symmetry-forbidden for ground states and symmetry-allowed for excited states.

To derive a general rule, one may enumerate, say, bonding symmetric levels in reactants and products. If there are, for example, \( m \) \( \pi \) orbitals in a reactant, there will be \( m \) \( \pi \) symmetric bonding \( \pi \) orbitals if \( m/2 \) is even, or \( m = 2n+1 \) if \( m/2 \) is odd. That part of the product derived from this component will contain \( m-2 \) \( \pi \) orbitals, of which \( m/4 \) are symmetric bonding levels if \( m/2 \) is even, or \( m-2 \) if \( m/2 \) is odd. There are three possible cases (\( m=4q \), \( m=4q+2 \), \( m=4q+3 \))

<table>
<thead>
<tr>
<th>Case</th>
<th>( m )</th>
<th>( n )</th>
<th>Total Symmetric Bonding ( \pi ) Levels Before</th>
<th>Total Symmetric Bonding ( \pi ) Levels After</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>( 4q )</td>
<td>( 2q )</td>
<td>( 2q )</td>
<td>( 2q )</td>
</tr>
<tr>
<td>2</td>
<td>( 4q+2 )</td>
<td>( 2q+1 )</td>
<td>( 2q+1 )</td>
<td>( 2q+1 )</td>
</tr>
<tr>
<td>3</td>
<td>( 4q+3 )</td>
<td>( 2q+2 )</td>
<td>( 2q+2 )</td>
<td>( 2q+2 )</td>
</tr>
</tbody>
</table>

Of the new bonding \( \pi \) levels in the product, one is always symmetric; thus, for a thermal symmetry-allowed reaction, the total number of occupied symmetric \( \pi \) bonding levels in the reactants must exceed by one the number in the product; Case 2 satisfies this condition: for it,

\[ m_{\text{total}} = 4q + 1 \] \( \text{or} \) \[ 4q + 2 - 4q + 1 = 2 \]

Cases 1 and 3 necessarily lead to bonding-antibonding correlations; consequently, thermal reactions in which

\[ m = 4q - 2 \text{ or } 4q - 2 \text{ or } 4q + 2 \text{ or } 4q + 3 \]

are symmetry-forbidden. In each case, the rules are precisely reversed for reactions involving excited states. Further, it must be emphasized that these conclusions apply only to cases in which the geometry of the reacting molecules is that specified above; we shall demonstrate in the sequel that in some cases the same, and in others different, rules apply when the geometric relationships within the transition state are varied.

3.1. General Comments on the Construction of Correlation Diagrams

A crucial phase in the construction of a correlation diagram is the identification of pertinent \( \sigma \) and \( \pi \) levels and their delocalization to the full extent required by the transition state symmetry. The simplest procedure may be formulated as follows:

a) Identify all orbitals involved as \( \sigma \), \( \pi \), or \( \sigma^* \) (nonbonded pair). Remember that for each \( \sigma \) and \( \pi \) level there will be corresponding \( \sigma^* \) and \( \pi^* \) levels; this is not the case for \( \sigma \) orbitals. Thus, for the expulsion of carbon monoxide from cyclopentadiene (19) the relevant orbitals are: in the cyclopentadiene the \( C-C \) \( \pi \) and \( \pi^* \) levels, two bonding \( C-C(=O) \) \( \sigma \) levels and the corresponding \( \sigma^* \) orbitals, and a lone pair on oxygen: in the products (20) and (21) the four \( \pi \) levels, two of which

However, if only fragments of a polyene system participate in a reaction, the molecular orbitals of the component fragments must be used. Thus, the conversion of a butadiene (23) to a bicycle(2,3,4)hexa-2,5-diene (28) or to a

\[ \sigma \] and \( \sigma^* \) must be transformed as indicated in (29), to \( \pi \) and \( \pi^* \) and \( \pi^* \).

Again consider the \( \sigma \) orbitals of cyclopentadiene (30).

\[ \sigma \]

\[ \pi \]

\[ \pi^* \]

\[ \pi^* \]
A similar mixing is required for noncoplanar π levels. Thus, in considering a [2+2] cycloaddition within 1,5-hexadiene, leading to a bicyclohexene, the preparation of π orbitals is performed as shown in (31).

A convenient, but not necessary, further step is to mix with each other all orbitals of a given symmetry. For example, consider the π bonds of a [2+2+2] cycloaddition of a cyclohexene to three ethylenes. Assume a boat conformation of the cyclohexene. The three localized π orbitals are $\pi_1$, $\pi_2$, and $\pi_3$ (32). The only symmetry element in the transition state is a plane bisecting $\pi_1$. The orbital $\pi_3$ is symmetric under reflection in this plane, but $\pi_2$ and $\pi_3$ are not. Thus, in accordance with rule a), above, we should form the delocalized combinations $\pi_2+\pi_3$ and $\pi_2-\pi_3$. This yields a new set of symmetry-adapted orbitals (33).

More extensive delocalization (a secondary effect — but one which can be of chemical significance) would follow from mixing of $\pi_1$ and $\pi_2-\pi_3$, and $\pi_2+\pi_3$ into the symmetric combinations.

3.2. Precautions in the Construction of Correlation Diagrams

There are several pitfalls in the construction and application of correlation diagrams. To avoid these the following precautions must be observed:

a) Each basic process must be isolated and analyzed separately. Otherwise the superposition of two forbidden but independent processes may lead to the erroneous conclusion that the combined process is symmetry-allowed. Two wrongs do not make a right.

b) The symmetry elements chosen for analysis must bisect bonds made or broken in the process. Here there are two considerations:

i) a symmetry element of no use in analyzing a reaction is one with respect to which the orbitals considered are either all symmetric or all antisymmetric — obviously an analysis based on such elements only (such as plane $3$ in the approach of two ethylenes [27] Figure 5) would lead to the conclusion that every reaction is symmetry-allowed;

ii) if the only symmetry element is one which does not bisect any bonds made or broken, then the correlation diagram constructed on the basis of this element can only lead to the conclusion — often false — that a reaction is symmetry-allowed.

c) Each case must be reduced to its highest invariant symmetry. Thus, if there are heteroatoms in a polyene component, they are to be replaced by their isoelectronic carbon analogues. If there are substituents with trivial electronic demands they should be replaced by hydrogens. Heteroatoms do offer the possibility of new reactions by the inclusion of nonbonding pairs or by the availability of low-lying unoccupied orbitals. These types of interaction should be carefully analyzed.

To consider an example of a), take the formation of ethane from cyclooctatetraene in one step (Figure 14).

Construction of a correlation diagram (Figure 15) without regard to precaution a) would lead to the conclusion that this superposition of two [2+2] cycloadditions should be a symmetry-allowed thermal process.

In fact the diagram should really appear as in Figure 16. The intended correlation of the $sp^3$ orbitals formed from $\pi_{3,4,5,6}$ is to an antibonding $sp^3$ orbital formed from $\pi_{3,4,5,6}$. A small perturbation links the $3,4,7,8$ cycloaddition with the 1,2,5,6 process. The latter by an accident of symmetry is forming an $sp^3$ orbital of the carbene. The result is that the intended bonding-antibonding correlation is accidentally avoided, but the reaction is none the less symmetry-forbidden. In fact, whether a reaction is symmetry-allowed or forbidden is determined by the breadth of the electronic hill that resonant or product orbitals must climb in reaching the transition state; and the presence or absence of a hill is a function of the involved correlation, or the initial
slope of the levels. From this point of view, we see that in the case at hand the 3-4, 5-4 combination is in no wise facilitated by the concurrent 1-2, 3-4 process, and vice versa.

An example of type b) is provided by consideration of the conversion of butadiene (33) to bicyclobutane (36). Here the only molecular symmetry element is a two-fold axis passing through a single bond which is not made or broken during the reaction. We will discuss this reaction in some detail in the sequel.

Another instance is the case of two propylenes trading hydrogen ([(37) - (38)], where only a center of symmetry (passing through no bonds) could be present.

Still another example is the decomposition of propylene to diacetylene and two acetylenes ([(39) - (40)], where no element of symmetry bisects bonds broken or made.

The rationale for point c) will become apparent upon comparison of the correlation diagrams for the face-to-face addition of ethylene to ethylene with that for ethene.

![Figure 17](image)

Figure 17. Left: Correlation diagram for the cycloaddition of two ethylene molecules. Right: Isomeric correlation diagram for the cycloaddition of ethylene to propene.

4. The Conservation of Orbital Symmetry

It is clear that the absence or presence of molecular symmetry in an absolute sense cannot be the ultimate source of the allowedness or forbiddenness of a reaction. Symmetry is discontinuous. It is either on or off, here or not here. Chemistry is obviously not like that. A slight perturbation, say substitution by a methyl group, may destroy total symmetry, but cannot be expected to change dramatically the mechanism of a reaction. The essential and decisive factor in making a reaction forbidden is that in the transition state there is at least one level that is no longer bonding, but at considerably higher energy. We have used symmetry as a method to aid us in determining these high energy levels without doing the least bit of calculation. If symmetry is lacking, either as a result of trivial substitution, or more basically from the geometry of the components (e.g., in the "constrained" reaction, a reaction may still be analyzed by writing down the orbitals involved, allowing them to mix according to well-defined quantum-mechanical principles and following the interacting orbitals through the reaction. High energy levels in the transition state may arise partly from real weakenings or from intended but avoided ones. Such high energy levels will not be present if every bonding orbital of the product (reactants) is derivable from one bonding orbital of the reactants (product). For if a bonding orbital of the product is not derivable from any bonding orbital of the reactants, it must related to the antibonding orbital of reactants. Whether or not it actually correlates to that antibonding orbital is dependent on the presence or absence of total symmetry: but even if the intended correlation is broken, the level appears to high energy in the transition state.

In short, the most general, and at the same time physically most realistic view of orbital symmetry control of chemical reactions is obtained by specifying the relevant molecular orbitals of reactants, and observing their corresponding forms in products, as reaction occurs with conservation of orbital symmetry. To illustrate our method we will first discuss some instances where correlation diagrams can be drawn, one of these in great detail, and then proceed to less symmetrical cases where no help may be expected from molecular symmetry.

5. Theory of Electrocyclic Reactions

These intramolecular cyclizations provided the stimulus for our study of molecular orbital symmetry and concerted reactions. We define as electrocyclic reactions the formation of a single bond between the termini of a linear system containing 4 π electrons, and the converse process (41).

![Figure](image)

Figure 18. Correlation diagram for the cycloaddition of ethylene to propene.

In such changes fixed geometrical isomerism imposed upon the open-chain system is related to rigid tetrahedral isomerism in the cyclic array. A priori, this relationship might be diastereotopic or conrotatory (42). In the former case the transition state is characterized by a plane of symmetry while in the latter a two-fold axis of symmetry is preserved.

Consider the essential molecular orbitals in the conversion of cyclobutene to butadiene. These are the four π orbitals of the butadiene 7, 2b, 2a, the H and π-levers.
els of the cyclohexene double bond, and the $\pi$ and $\sigma$ orbitals of the single bond to be broken (43).

Consider carrying out a conrotatory motion to completion on $\sigma$ (step 1 in (44)) and follow through with a erythromycinization (step 2). At this stage the orbital looks like a segment of $\pi_2$ (or $\pi_4$) of butadiene and all that is needed is a growing-in (step 3) of orbitals at C-2 and

C-3.

It should be kept in mind that in reality the steps 1, 2, and 3 will all be simultaneously proceeding along the reaction coordinate, and that the above factorization is only an aid to visualization. The growing-in of step 3

may seem like magic to those unfamiliar with molecular orbital manipulations. It is in fact a universal phenomenon, the detailed result in this case of mixing of $\pi^*$ with $\sigma$ as the reaction proceeds. We have now followed $\sigma$ through the reaction and correlated it with another bonding orbital, $\pi_2$. Similarly we follow $\pi$ through (45). Note here that the growing-in step 3 is really a mixing of $\pi$ with $\sigma^*$ (cf. step 6), $\pi$ thus correlates with $\chi_2$.

The correlations could of course have been obtained starting from butadiene. $\pi_2$, by acyclic rotation becomes $\pi$ (46) and $\pi_3$ is transformed into $\sigma$ (47).

In this analysis there appears a fading-away, in which extra nodes and contributions disappear. This is the precise reverse of the growing-in noted above and it again a result of mixing with higher orbitals of the proper symmetry. Very similar arguments lead to a correlation of $\sigma^*$ and $\chi_1$, and of $\pi$ and $\pi_3$ and $\chi_1$.

We have thus achieved a correlation of bonding levels of the reactant with bonding levels of the product, with conservation of orbital symmetry. The thermochemical reaction should be a facile one.

By contrast, consider now a disrotatory opening. The correlations are indicated in (48). Both $\sigma$ and $\pi$ must correlate with $\pi_1$ of $\sigma_3$ (=$-\pi_3$). But since only one can correlate with $\pi_1$, the other must go up to $\pi_2$, which it antibonds. Conservation of orbital symmetry requires in this case a high-lying transition state and the

thermal reaction is symmetry-forbidden. Again the problem could have been approached from the other side (49).

It is obvious that $\pi_2$ is the troublesome orbital — it cannot transform into any bonding orbital of the cyclohexene, with conservation of orbital symmetry, in a disrotatory process.

What we have somewhat laboriously described in words is equivalent to the construction of two-level correlation diagrams (Figure 19). It is clear that the conrotatory process (a two-fold rotation axis) is maintained at all times whereas the disrotatory motion an invariant plane of symmetry is present. These diagrams are clearly analogous to those discussed in section 3 (above) for combination reactions of $\pi$ electrons. Obviously the diagram for the conrotatory process is characteristic of a symmetry-forbidden reaction, while the pattern for the disrotatory process is that of a symmetry-forbidden reaction.

We should emphasize at this point that this detailed stepwise analysis has been presented primarily for pedagogic reasons. The high molecular symmetry present in these cases would have permitted very simple direct derivations of the relevant correlation diagrams. But soon we will encounter cases of such low symmetry that the stepwise analysis is the only possible one.

The highest occupied orbitals play a dominant role in these correlations. Their importance is easy to justify. First, we think of them as containing the valence electrons of the molecule, most easily visualized in incipient reaction. In this sense their role has been stressed in the important work of Fukuoka. Second, if there is little symmetry in a molecule and if there is a bonding level which is intending to cross the energy
The disrotatory process pushes a plus lobe onto a minus lobe. Since one end of the molecule "feels" the phase of the wave function at the other end, this is an antibonding, destabilizing interaction. The level moves up in energy along the reaction coordinate. Conrotatory motion brings a plus lobe onto a plus lobe (or minus on minus, which is equivalent). This is a bonding, stabilizing interaction terminating in the actual formation of the new σ bond.

A warning note should be sounded here. The sense of orbital symmetry control of any concerted reaction can always be determined through inspection of the behavior of the highest occupied molecular orbital in the reaction system, but the analysis is often less simple than it is in the case of the butadiene → cyclobutene transformation. A temptation especially to be avoided in making such analyses is that of inadvertently placing more than two electrons in a single molecular orbital.

Figure 19. Correlation diagram for the disrotatory and conrotatory motions in cyclopropane.

The disrotatory motion is a good example of a case where the actual formation of the new σ bond need not be the end of the story. The disrotatory motion may be followed by a rotation of the ring, leading to the formation of a new bond. This is known as the "tobacco" motion. The net result is the formation of a new bond, and the ring is twisted by 90°.

Several conclusions follow. If R in (53) or (54) is some bulky group then we should expect the stereochemistry of the products to be conrotatory for (53) and disrotatory for (54). On the other hand, when R is a small group, then we should expect the equal- 

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Figure 20. Conrotatory and disrotatory modes of approach.

Figure 21. Conrotatory and disrotatory modes of approach.

Figure 22. Conrotatory and disrotatory modes of approach.

Figure 23. Conrotatory and disrotatory modes of approach.

Figure 24. Conrotatory and disrotatory modes of approach.

Figure 25. Conrotatory and disrotatory modes of approach.

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Figure 26. Conrotatory and disrotatory modes of approach.

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Figure 27. Conrotatory and disrotatory modes of approach.

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Figure 28. Conrotatory and disrotatory modes of approach.

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Figure 29. Conrotatory and disrotatory modes of approach.

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Figure 30. Conrotatory and disrotatory modes of approach.

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Figure 31. Conrotatory and disrotatory modes of approach.

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Figure 32. Conrotatory and disrotatory modes of approach.

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Figure 33. Conrotatory and disrotatory modes of approach.

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Figure 34. Conrotatory and disrotatory modes of approach.

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Figure 35. Conrotatory and disrotatory modes of approach.

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Figure 36. Conrotatory and disrotatory modes of approach.

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Figure 37. Conrotatory and disrotatory modes of approach.

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Figure 38. Conrotatory and disrotatory modes of approach.

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Figure 39. Conrotatory and disrotatory modes of approach.

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Figure 40. Conrotatory and disrotatory modes of approach.

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Figure 41. Conrotatory and disrotatory modes of approach.

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Figure 42. Conrotatory and disrotatory modes of approach.

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Figure 43. Conrotatory and disrotatory modes of approach.

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Figure 44. Conrotatory and disrotatory modes of approach.

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Figure 45. Conrotatory and disrotatory modes of approach.

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Figure 46. Conrotatory and disrotatory modes of approach.

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Figure 47. Conrotatory and disrotatory modes of approach.

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Figure 48. Conrotatory and disrotatory modes of approach.

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Figure 49. Conrotatory and disrotatory modes of approach.

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Figure 50. Conrotatory and disrotatory modes of approach.
to the ring to be severely disfavored, since the resulting rotation would lead to a trans,trans-alkyl cation in a small ring. We should expect a facile opening only for a

The half-life of (58) decreases for small $n$ since, due to ring strain, the reaction itself becomes highly exothermic.

5.1. Electrocyclic Reactions Enamelled

The concerted electrocyclic change of a cyclobutene to a butadiene is a very well-known process. Its stereochemistry was established some years ago [64] and its scope and energetics have been very carefully studied [65]. Satisfactory rationalization of the striking stereospecificity of the reaction was lacking until the orbital symmetry control of electrocyclic changes was discovered. Given that in the thermal reaction concerted displacement is symmetry-allowed, it follows that

$$\text{cyclohexadiene} \rightarrow \text{cyclohexene}$$


[a] The bicyclic cyclobutene containing a cis-fused methylene chain (58) leads to a cyclic cis-trans-diene (59).

Such a trans-olefin becomes increasingly highly strained as the ring size diminishes. This trend is best

$$\text{cis-trans-diene} \rightarrow \text{cis-cyclohexene}$$


[b] The highly substituted butadienes (64) and (66) have been studied in most ingenious and amusing experiments [66]. These substances are equilibrated through the intermediacy of the cyclobutene (65). After fifty-five days at 124 °C each cyclobutene molecule had faintly undergone 2.6 ± 0.0 conjugate openings, and a disconjugated double bond was yet to appear.


One case with greater stereospecificity (71) has been observed [67] and fits our expectations.

$$\text{cis-cyclohexene} \rightarrow \text{cis-cyclohexane}$$


[h] Recently it has been confirmed that trans,trans-1,6-hexadiene undergoes photochemical cyclization to cis,trans-hexadiene [68]; the case is of special interest in that the spectroscopic constraints are absent.

The diastereomer (72) yields on photolysis the bicyclic isomer (73), which reverts readily to the

$$\text{cis-cyclohexene} \rightarrow \text{cis-cyclohexane}$$


A related reaction presumably also takes place in the photocyclization of cis-stilbene (74) and similar compounds.


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The electrolysis closure (83) of a cyclic-octaetamer should be thermally conrotatory, photochemically disrotatory. Through any conformation of a cyclic-octaetamer, the conformation of the octamer is preserved. The predicted stereochemical course of the thermal reaction has been confirmed recently.[30]

The preparation of the tautomer (83) by Grozinger[12] presents a situation of great interest, related to the octamer-cyclooctatetraene electrocyclic conversion. Undoubtedly, the substrate would suffer instantaneous transformation to its isomer 9,9'-bistriptyc. [86] In fact, 9% of 20 minutes at 90 °C were not for the circumstances that the symmetry allowed conrotatory transformation is opposed by a necessary concomitant and, difficult, twisting motion about the 9,9'-double bond, while the geometrically simpler disrotatory cleavage is symmetry-forbidden.

A detailed study of all methyl-substituted cyclopropyl trimethanes clearly showed the steric effects of methyl groups forced against each other by the steroelectronic factor.[31]

Since then, numerous further confirmations have appeared. We mention here only two of these. Grozinger and co-workers[12] observed the reactions [92], and Whittington has shown that closure of endo-hydroxyxanthene[3.1.0]dioxane gives the expected transient cyclooctatetraene[93].

The electrocyclic closure of the cyclopropyl anion has not been tested directly in the parent case, but an isolatrotropic example, drawn from aziridine chemistry, provides a striking confirmation of the conservation of orbital symmetry. The beautiful observation of Hunig, Scheer, and Meier[13] are summarized in the diagram (94).

The 1,3-dipolar isomer of an aziridine is a 4,4-electron molecule which is not conrotatory to allylic anion. The net inversion of stereochemistry observed in the thermal reaction would be extremely puzzling if it were not the obvious consequence of a conrotatory opening, followed by a [4+2] cyclodaddition.

The cyclization of perfluorinated cations cyclopentenyl ions is a reaction extensively studied by Derno and by others. In the present study, we have shown that the reaction is not conrotatory to allylic anion. The net inversion of stereochemistry observed in the thermal reaction would be extremely puzzling if it were not the obvious consequence of a conrotatory opening, followed by a [4+2] cyclodaddition.
The stereochemistry of the reaction has been established in recent studies at Harvard.[51] Treatment of disphysicalyl ketone (96), R = H, with phosphoric acid affords two ketones (98), R = H, and (99), R = Me, together with (95), R = Me; in this case the process is not complicated by oncometabolism formation of a stereocentrially uninformative product of type (97). Thus, the predicted conrotatorial course is cleanly followed in both cases. Moreover, the irradiation of (95), R = H, yields a ketone (98) which is the product of disrotatory cyclization.

The opportunity for observing the exact state reactions of disphysicalyl cation (99), generated mass spectrometrically, cyclizes to a hydroxylketone species which loses hydrogen atoms one at a time, and is thus probably the trans ion (102) — again the result of the symmetry-allowed excited state process.

Chopin and his co-workers have observed photochemical cyclizations of the allyl ketones (103). These are isoelectronic with pentadienyl anions, and their excited state closure should take a conrotatory course. The initially formed intermediate (104) apparently returns to the ground state and undergoes a hydrogen shift in symmetry-allowed suprafacial [4,4] diastereoslective — see Section 7) leading to the stable final product (105).

Very recently, the first example of the electrophilic closure of a simple cyclohexadienyl anion has been observed.[52,53] X-ray Analysis has studied an exceptionally interesting system in which triple and double cyclic elecrocyclization processes are operative.[47] When one electron is added to cyclohexane (106), a suprafacial [3,3] diastereoslective — see Section 7) process is produced, clearly with symmetry-allowed diastereomeric geometrical dispositions. Moreover, yet another electron can be added, to give a ten-electron doubly charged anion. In spectacular contrast[48], addition of an electron to the isomeric trans-trisene (107) is not accompanied by decompartmentalization of the cyclopropane

A similar sequence of electrocyclization reactions is provided by the pyrolysis of oxacyclohexene (108) to the isomeric[49] trans-1,3,5-triethylenecyclohexane (110) which serves thermally to the cis-9,10-dihydronaphthalene (111). In these reactions, the symmetry-allowed [3,3] migratory shift (see below, Section 7) and a four electron conrotatory electrocyclization reaction.

The recently synthesized[50] 16-allyl-18-methyl-17-cyclohexadiene isomerizes thermally and photochemically to two different isomers[50], whose products of double disrotatory and double conrotatory closure, respectively, of very special interest is the recent discovery of metal catalyzed electrophilic cyclizations. For example, the dibenzobarrelene (112) is observed to undergo thermal isomerization to dibenzobarrelene (114) when heated at 180°C for 4–5 hours[51]. A forbidden disrotatory opening (112) → (114) is here obviously made allowed by the extra orbitals and electrons available from the complexing metal ion. A similar steric interference of the rules for cycloaddition and cycloreactivity

References:
[56] K. H. Dieter, unpublished observations.
6. Theory of Cycloadditions and Cycloreversions

In our discussion of correlation diagrams, we have already derived the selection rules for one type of simple two-component cycloaddition, namely, that which is suprafacial on each component. A suprafacial process is one in which bonds made or broken lie on the same face of the system undergoing reaction. For example, in an ethylene (122) or cis-cyclopropane (133), formation of bonds in the senses indicated by the arrows takes place in a suprafacial manner.

A priori, however, there are alternative, antisuprafacial processes, in which the newly formed or broken bonds lie on opposite faces of the reacting systems (130) and (131).

We shall use the terms suprafacial and antisuprafacial to designate those geometrical alternatives in making general allusions to reaction types, and the letters a and asubscripts to define particular reactions. Thus, the cycloadditions mentioned above are suprafacial reactions, and the Diels-Alder reaction is a [4+2] process (131).

A priori, there are in fact four possible modes of combination of the terms of two surface components in a cycloaddition reaction. Each mode has a characteristic stereochemical consequence, as displayed in Figure 21.

In using the principle of orbital symmetry, we can determine whether any cycloaddition is suprafacial and dissymmetrical (131). The terms suprafacial and antisuprafacial were first used in our discussion of supramolecular reactions (132).

We shall illustrate the procedure for all possible [2+2] reactions. In each case, the four relevant electrons are placed in pairs in the two generalized cyclobutane orbitals (136) and (137).

The reaction is symmetry-allowed.

b) The [3+2] process. When the α electrons are cleared, the two electrons in the orbital (138) can pass with symmetry conservation into a bonding orbital (139) of one ethylene molecule, while those in (137) can only enter an antibonding orbital (140) of the other ethylene.

The reaction is symmetry-forbidden.

c) The [2+2] process. When the β electrons are cleared, the two electrons in the orbital (136), now shown distorted in a purely formal manner, can pass with symmetry conservation into a bonding orbital (140) of one ethylene molecule, while those in (137) likewise pass into a bonding orbital (141) of the other ethylene.

The reaction is symmetry-forbidden.

- The [2+2] process. When the β electrons are cleared, the two electrons in the orbital (136), now shown distorted in a purely formal manner, can pass with symmetry conservation into a bonding orbital (140) of one ethylene molecule, while those in (137) likewise pass into a bonding orbital (141) of the other ethylene.

We shall illustrate the procedure for all possible [2+2] reactions. In each case, the four relevant electrons are placed in pairs in the two generalized cyclobutane orbitals (136) and (137).

The reaction is symmetry-allowed.
The reaction is symmetry-forbidden. It will be noted that this analysis just completed reveals the existence of a concerted symmetry-allowed path for the combination of two ethylene compounds to give a cyclobutene. With the simplified formal analysis does not render obvious is the actual geometry of approach for the allowed [2 + 2] process, which clearly must differ from that of the symmetry-forbidden combinations. When one considers in detail the manner in which maximum overlap of the relevant orbital lobes may be achieved in the [2 + 2] reaction, it is clear that the ethylene components must approach one another orthogonally, as in (144).

It is further worthy of comment that a complete correlation diagram may be constructed for the allowed [2 + 2] reaction, using a two-fold axis of symmetry which passes through the midpoints of both of the ethylene bonds. Similar circumstances obtain in the case of the [2 + 2] reaction. In this case the geometry of approach is that shown in (145), and the reaction is forbidden in the ground state, as deduced above, but allowed for the excited state (cf. Figure 22). A final point of much importance is that the principle of conservation of orbital symmetry is valid, whether or not a formal correlation diagram can be constructed. For example, no pertinent correlation diagrams can be drawn for the concerted [2 + 2] and [6 + 2] combinations, but orbital symmetry analysis readily reveals that the former is forbidden and the latter allowed. The generalized cycloaddition rules are now easily derived. In the addition of an electron to an electron system the rules shown in Figure 22 must be observed for concerted processes (e.g. in a + 3). The rationale underlying these important conventions will be apparent immediately upon consideration of additions to an ethylene molecule, regarded as containing two π bonds.

a) As shown in Figure 23: superfacial on the π bond. For the n bond, i.e. [2π + 2n].
b) As shown in Figure 24: superfacial on the π bond. Subfacial on the π bond, i.e. [2π + 2π].

It will be observed that whichever formal view is taken, the corresponding processes represent symmetry-allowed cycloaddition reactions; by contrast, the corresponding analogous must be regarded as [2π + 2π] or [2π + 2n] reactions, which are, of course, symmetry-forbidden in ground states.

As a final illustration we may now characterize the concerted scission of cyclobutene as a [2π + 2n] process.

6.1. Cycloadditions and Cyclorotations Exemplified

The [2 + 2] cycloaddition is one of the most widely observed photochemical reactions, with more than one hundred examples quoted in a recent review. It is likely that many of these reactions are not concerted, probably as a consequence of the fact that competitive relaxation of a participating excited state exists, with transformation to an equilibrium geometry in which the ethylene moieties are 90° out of coplanarity. Thus, trans-fusions are common in many of the cycloadducts; of course, it should be noted that trans products would result from concerted symmetry-allowed [2π + 2n] combinations of vibrationally excited ground-state molecules. Nevertheless, two striking examples of concerted symmetry-allowed photo-induced [2 + 2] processes have recently been observed. Thus, irradiation of the trans-1,3-dienes 2-butenes, separately and in admixture, gives the results shown in (156).
Further, a pretty example of the photochemical \([2+2]\) reaction has been discovered.  

![Diagram 1](image1)

It is quite possible that the reversal of the simplest \([2+2]\) cycloaddition, the pyrolysis of cyclobutane, is not a concerted process. The pre-exponential factor of the Arrhenius equation has been regarded as consistent only with a stepwise decomposition through a tetramethylene radical. Further, the fact that pyrolysis of cis- or trans-dimethylcyclobutane (112) yields a mixture of cis- and trans-butenes, among other products, has been adduced in support of the diradical mechanism. Nevertheless, if the cycloreversion is concerted, it must be of the type \([2+2,2\rightarrow1]\), and the same steric factors should be observed.

![Diagram 2](image2)

A beautiful example of the symmetry-allowed \([2+2,2\rightarrow1]\) combination has been discovered by \[149\].

![Diagram 3](image3)

It is worthy of note that when a double bond is twisted about its axis — as it must be in (113) and (115) — the concomitant orbital twisting is such as distinctly to favor the \([2+2,2\rightarrow1]\) process.

A further interesting point which emerges from a detailed consideration of the general case (Figure 25) is that the reaction-facilitating twisting motions generate systems of opposite chirality in the two ethylenic components. Consequently, we may predict that the optical intermediary of (160), which closes in a testable fashion to the observed product. The decisive experiment was recently reported by Chase and Pfeffer [150]. Their results are summarized in (162).

![Diagram 4](image4)

Remarkably, there exists in principle an alternative pathway relating bicyclobutane and butadiene, with precisely opposite sterochemical consequences. This route \([113] 
([154] 
(157)]

may be described as involving symmetry-allowed \([2+2,2\rightarrow1]\) and \([2+2,2\rightarrow1]\) reactions. The possibility that special substitution patterns — perhaps operating through attendant steric effects — may bring this path to light should surely be admitted. The reaction may find itself illuminating to verify for itself the relationship displayed in Figure 26, which presents the stereochemical pattern for all possible symmetry-allowed processes relating bicyclobutanes, cyclobutanes, and butadienes.

![Diagram 5](image5)

The number of known Diels-Alder reactions — the \([2+4]\) cycloadditions — is legion [154, 157]. Through a diradical mechanism, it has been advanced on numerous occasions [154], the overwhelming body of experimental facts is consistent only with a concerted mechanism [157].

There is a growing body of photochemical Diels-Alder reactions [158], but in most instances there is no evidence which provides information as to whether the reactions are concerted or not. However, it may be void that concerted symmetry-allowed excited-state \([2+4]\) processes are involved in the ubiquitous conversion of

![Diagram 6](image6)

**Figure 26.** Symmetry-allowed processes relating bicyclobutanes, cyclobutanes, and butadienes. — Alkenes assumed pure para. — Alkenes assumed equal para and meta.
No reaction involving a substance sufficiently extensively labeled as to provide a test of these considerations has been studied. In vitamin D3, the top and bottom faces of the steroid ring system are no longer equivalent, and the processes which lead in the general case to the labeling of the starred atoms is not possible to discern whether the 9α system participates in the reactions in a superficial manner.

A proposed mechanism for the observed transformation of the products 185-187 is the following: the reaction 187-185 proceeds via the intermediate 188, which is then converted to the final product 185.

At elevated temperatures, in the presence of base, acetophenone (189) is smoothly converted to acetone (190). In a similar manner, at 200°C, the corresponding reaction 184-183 takes place readily.

With the acetylenic ester, protection as an enamine by way of an enamine salt is possible, but no information is available about the detailed mechanism of the reactions.

Cycloaditions are well known. As yet, they have encountered only in photochemical reactions, and no detailed stereochemical information is available.

[4-6] Cycloaditions are relatively frequently observed. Hemisulfur (186) readily combines with dimethyl acetylenedicarboxylate (193) to give (187), whereas sulfur (188) does not react in a similar way because the reaction is symmetry-forbidden.

Cycloaditions are known to be used as intermediates in organic synthesis, and the fact that the product (189) fails to undergo cycloaddition to benzene and

Conclusion: The proposed mechanism for the observed transformation of the products 185-187 involves the symmetrical allowed 9α system participates in the reactions in a superficial manner.

Two kinds of cycloaditions, discovered by Beckwith, are portrayed in (191) and (192).

Cycloaditions were unknown until our elucidation of the principle of orbital symmetry conservation stimulated the search for them. The cases (193) - (198) are now known.


Cycloadditions involving cationic components are as yet not common. Ionic [2+2] cycloadditions may be realized in a number of different ways ([203]→[204]).

We may assign to class A, the cycloaddition reactions of cyclopropanes (205). It is not unlikely that cyclopropanes are in equilibrium with an isomeric dipolar species. The latter can act as a 2π-electron system, and, predictably, combines with dienes in [4+2] processes — for example, with furans to give adducts of the type (206) [108].

Most recently, the direct combination of the 2-methyl-allyl cation (207) with cyclopropanes and with cyclohexadiene, to give the bicyclic cations (208), 2-(CH$_2$) or -CH=CH-C$_2$H$_5$, has been demonstrated [109].

A remarkable cycloaddition of class B is that which occurs in the formation of the pinitro[209] from pentaerythritol (209).

As yet, no simple instances of class C involve [2+2] cycloadditions have been discovered. However, very important and numerous groups of reactions — the 1,3-dipolar additions [110] — may be placed in this class, since the 1,3-dipolar substances which participate in cycloaddition reactions, although formally neutral molecules, generally function as three- or four-electron species. Halogen, whose own magnificent researches have transformed 1,3-dipolar addition from an obscure phenomenon, exemplified only by a few curiosities, into a major reaction-type, has prepared excellent surveys of the field [111], and has analyzed the process in terms of orbital symmetry conservation [112]. Consequently, it is only necessary here to summarize briefly the major fundamental factors, and to allude to a few special points. The great majority of known participants in 1,3-dipolar addition reactions are isoelectronic either with ozone (210) or with nitrosy oxide (212), and unambiguously contain a three- or four-electron system occupied by six electrons.

Another class of reactants is represented by labile molecules which undergo ready transformation into species containing the requisite 4-electron system, e.g., the carbonyl ylides (214) and the azomethine ylides (216) are produced by electron transfer from ethylene oxides (213) and ethylene imines (215), substituted in such wise as to facilitate ring closure, the

6.2. [2+2] Cycloadditions in the Photochemistry of the Cyclohexadienes and Cyclohexenones

Following the ground-breaking work of Bancroft, Jeger, and their co-workers, the beautiful complexity of the photochemistry of cyclohexadienes and cyclohexenones has been most fully explored by Chapman, Schaeffer, Schonbrun, Zimmerman, and their collaborators [113].

The primary isomerization processes which have been noted are of three types (221) and (222).

It seems probable that all, and has been established that some, of these cases involve reactions proceeding through an optical triplet state. It has also been clearly established that the quantum efficiency of the processes varies over a very wide range (108). Detailed mechanisms have been proposed for these reactions (210-213), the most elaborate and ingenious of these mechanisms is that suggested by Zimmernann (211).

We would like to examine the stereochemical constraints imposed by conservation of orbital symmetry on these transformations. These constraints are operative only if the reactions are concerted. We are aware of the elegant physical measurements which have been interpreted as supporting the proposed non-concerted mechanisms. But we regard it as worth while to stipulate the stereochemical implications associated with concerted pathways from the starting materials to the observed products.

Formally, all of the reactions are of type (a) or (b). In classes A (and B) there are two distinct pathways, depending on whether the addition at C-4 is on the top or bottom. In A and B there are different substituents these pathways become distinct, each with its own steric factors. It is this likely to give an energetically favorable process and yield products in differing proportions. The products of inversion are diastereomeric, and enantiomeric to the products of retention. The actual course followed in the rearrangement of a chiral double bond is not yet known.

The molecules (222), (223), and (224) are all products of type (a), i.e., products previously discussed in a symmetrical manner. It is generally to be noted that inversion must occur at C-4 during each of the photoisomerizations. For the substitution patterns (a) and (c) only one product is expected (222) of the two which might result from symmetry-allowed changes involving the 2,3 double bond is observed. Similarly, only (224) is produced (from 2,4 and 2,5) where the 5,6 double bond is implicated. In the case of (d), three of the four possible products of symmetry-allowed processes have been isolated. Not one of the four products which might result from symmetry-forbidden or non-stereoselective processes has been found.

Unfortunately, the Zimmernann mechanism (110) for reactions of class A, illuminated with the insight afforded by orbital symmetry considerations, leads to precisely the same products which must be obtained in a concerted reaction. For readers (221—222) show the basic mechanism suggested by Zimmernann (211).

The final step, following bond reorganization (221—222), is a symmetry-forbidden (230a—230b) rearrangement; note that inversion (227c) to the original cyclohexadiene (222) (cf. arrows in 223a—223b) is symmetry-forbidden. There are actually two possibilities for the last step of this sequence. They are best described as 1,2 and 1,4 sigmatropic shifts (cf. Section 7, below). The first process consists of two non-symmetric [1,2] shifts (220b) (224c) (224c) (224d), while the second is a [1,4] rearrangement (222c) (224c) (224d). Since [1,2] sigmatropic shifts must proceed with retention, but [1,4] shifts, if forced to be suprafacial, must proceed with inversion in the migrating carbon, it follows that the consequences of the two alternatives are stereochemically indistinct.

The molecules (222), (223), and (224) are all products of type (a), i.e., products previously discussed in a symmetrical manner. It is generally to be noted that inversion must occur at C-4 during each of the photoisomerizations. For the substitution patterns (a) and (c) only one product is expected (222c) of the two which might result from symmetry-allowed changes involving the 2,3 double bond is observed. Similarly, only (224c) is produced (from 2,4 and 2,5) where the 5,6 double bond is implicated. In the case of (d), three of the four possible products of symmetry-allowed processes have been isolated. Not one of the four products which might result from symmetry-forbidden or non-stereoselective processes has been found.

Unfortunately, the Zimmernann mechanism (110) for reactions of class A, illuminated with the insight afforded by orbital symmetry considerations, leads to precisely the same products which must be obtained in a concerted reaction. For readers (221—222) show the basic mechanism suggested by Zimmernann (211).

The final step, following bond reorganization (221—222), is a symmetry-forbidden (230a—230b) rearrangement; note that inversion (227c) to the original cyclohexadiene (222) (cf. arrows in 223a—223b) is symmetry-forbidden. There are actually two possibilities for the last step of this sequence. They are best described as 1,2 and 1,4 sigmatropic shifts (cf. Section 7, below). The first process consists of two non-symmetric [1,2] shifts (220b) (224c) (224c) (224d), while the second is a [1,4] rearrangement (222c) (224c) (224d). Since [1,2] sigmatropic shifts must proceed with retention, but [1,4] shifts, if forced to be suprafacial, must proceed with inversion in the migrating carbon, it follows that the consequences of the two alternatives are stereochemically indistinct.
The photochemical rearrangement of cyclohexenes (the class B reactions) is a highly stereospecific process, and very probably follows a concerted course. Tuinstra found 1111 retention of chirality in the reactions (244) and (245).

Formulas (246) show the consequences of the stereochemically feasible reactions enantiomerically pure on the double bond with options of retention or inversion at C-2.

A steroidal derivative of this class has been photolyzed 1111. Of the two distinct possible products, only that one is produced whose cyclopropane ring is oriented (250). Since labels are lacking at C-3, the possibility of any question of retention or inversion is as yet unanswered. We predict that the reaction will be found to proceed with inversion at C-2. Similar circumstances obtain in the case of a further example (251) and (252) 1111.

There appear to be a number of examples of photochemically induced [2,2,1] cycloadditions involving simple olefins and dienes. Thus Griffin and coworkers 1111 observed unusual pericyclic cyclopropane cyclizations accompanied by group migrations (253) and (254). These could well be concerted transformations, but definitive stereochemical information is lacking.

An instance of this type of reaction in which the stereochemical course has been established is available in the photoysis of 4,4-diphenylcyclohexene (255) 1111. The predominating product is the result of an antarafacial addition on the double bond and inversion at C-4.

A related case (256) has been observed by Edgington 1111. A concerted cycloaddition may involve either the α bond at 3.7 (261) or that at 2.3 (262). The concerted nature of the reaction could be ascertained using a chiral reagent.

Still other reactions of this type are found in the conversion of a dibenzocyclo[2.2.2]octatetraene (262) to a dibenzobicyclo[2.2.2]octatetraene (263) and of a labeled hemi-bicyclo[2.2.2]octatetraene (264) to a hemi-bicyclo[2.2.2]octatetraene 1111.

[1112] D. Bellah and A. Schaffner 1112, studied the reaction with a very subtle probe; the insemination of (246) proceeds with retention at C-10 and inversion at C-10. The inversion at C-10 is forced by the steric situation, but the retention at C-1 is not, and is clearly consistent with a radical fragmentation of the C(1)-C(10) bond.


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We emphasize that neither of these cases need be concerned; indeed, there is evidence for a stepwise process in the corresponding reaction of the parent benzene (128).

We must now examine the question of how a process shown to proceed through an excited triplet state of a molecule could possibly be concerted. We believe that orbital symmetry relationships dictate to a molecule in an excited state a certain set of motions, leading to reactions, which are facile, and another set of motions which are difficult. There is no necessity to reach the excited state of products. The symmetry-allowed motions are initiated in the excited state of the reactant. In their course they are accompanied by a radiativeless transition to the ground-state of the product. While the physical rationale of such a transition is still lacking, the occurrence of such a process presents no more difficulty than does any other radiativeless transition.

6.3. The [2+2+2] Cycloaddition Reaction

Further useful practice in the application of the principle of orbital symmetry conservation may be gained from a detailed consideration of the [2+2+2] concerted cycloaddition (or cycloreversion) reaction; the exercise is made more valuable through the emergence from it of some new factors, and through the fact that it sets the stage for comparisons in the sequel, which deepen our understanding of orbital symmetry conservation as a fundamental extension of our knowledge of the phenomenon of chemical bonding.

Let us consider the decomposition of cyclohexane, through a boat-shaped transition state, into three molecules of ethylene. First, we assign six electrons —

which most explicitly reveal the largest extent of delocalization in the generalized molecular orbitals — in this case (265) and (267), rather than (270) and (271).

In any event, no other acceptable orbitals are available for the case at hand, and it is important to realize that in consequence there is no element of arbitrariness or of ambiguity in the conclusions we shall reach.

We next note that the six electrons in the π orbitals of the product ethylene molecules must be assigned to the generalized molecular orbitals (272)–(274).

One further, and very important, factor must now be recognized. The geometrical relationships among starting material and products, as revealed by inspection of (275), require that in the course of reaction, rotations —

about the axes 1, 2, and 3 must take place, in such wise as to bring the substituent groups at C-1 and C-2 on the one hand, and those at C-3 and C-4 on the other, into the common planes in which they lie in the respective product ethylene molecules. A priori, on purely geometrical grounds, three displacements might be corrosory (276) or disrotatory (277), and there are of course, in each case two possibilities (arrows in (276) and (277)).

Now we are properly prepared to annihilate our cyclohexane molecule. We shall see that there are two,

and only two, symmetry-allowed ways in which this decomposition may occur — given the transition state geometry we have chosen.

1. Let us first permit the two electrons in orbital (265) to enter orbital (272), as of course they may do with conservation of orbital symmetry. It is then at once clear that the two electrons in orbital (267) must occupy orbital (278) of the product array — and that of the 2001 total displacements enumerated above, the inwards disrotatory one (271) must obtain. It remains only to place the remaining σ pair — those in the orbital (266) and only two, symmetry-allowed ways in which this decomposition may occur — given the transition state geometry we have chosen.

Also of interest is the extent of reaction — into orbital (274) of the product assembly; a special point here is that pairing of the occupied orbital (266) with the unoccupied antibonding backbone σ* orbital (279) is consistent with the same inward disrotatory motion about axes 1, 2, and 3. The symmetry-allowed process which we have now depicted in full detail may be designated a [2+2+2] cycloreversion reaction. Naturally, a procedure analogous analysis applies to the reverse process — the symmetry-allowed [3+2+2] cycloaddition reaction.

2. Alternatively, let us first permit the two electrons in orbital (267) to take up new positions in orbital (272) and (274). Now those in orbital (265) have no choice but to enter orbital (273) of the product array. And, in sharp contrast to the case discussed above, the cleavage of the backbone bond (2,3) must be accompanied by outward disrotatory displacements (276). As before, the remaining pair, occupying orbital (266), takes up new positions in orbital (274), and, as before, mixing of (266) with the unoccupied antibonding backbone σ* orbital (280) is consistent with the outward disrotatory motion required by the symmetry relationships between orbitals (280) and (274). The process here delineated may be designated a sym-
will be considerably steeper for the s, a, a process of (283)→(284).

Several facets of the [2+2+2] reactions deserve further, if now briefer, consideration. The reader may wish to sharpen his apprehension of symmetry considerations through verifying for himself the propositions which follow:

a) There is a continuum of topologically equivalent symmetry-allowed thermal [2+2→2+2] processes, whose transition states vary from that depicted above to one whose geometry resembles that of a chair cyclohexane ring.

b) There are two further symmetry-allowed thermal [2+2→2+2] processes, topologically different from the one described above, which proceed through enantiomeric transition states possessing a two-fold axis of symmetry.

c) There are no symmetry-allowed thermal [2→2+2] processes.

d) There are no symmetry-allowed thermal [2→2+2] processes.

e) For reactions involving occupied antibonding levels - for example, reactions of molecules in photochemically excited states - there are no s, a, a, a, a, a processes.

f) Every all-unimolecular [2+2→2+2] combination of symmetry-forbidden in ground states, and symmetry-allowed for excited states in which the antibonding orbital of one participating ethylene unit is occupied.

Let any might cavil at the discussion of processes which on casual consideration could appear to be so improbable of realization as only to merit summary dismissal, we may allude to the essentially strain-free, as yet unknown, molecules (284) and (285), whose double bonds are constrained by the frameworks in which they are embedded as to favor photochemical conversion in (285) and (287), by the all-unimolecular paths mentioned above.

Further insight into the basic nature of symmetry-determined bonding relationships can be gained by simplifying our discussion of prismatic to a number of ways. First, let us note that, in a formal sense, the transformation of prismatic into benzene might be regarded as a [2→2+2→2] cycloversion reaction (300)→(301). We have seen in the preceding section that thermal reactions of this class are symmetry-allowed. What then excludes the prismatic-benzene

It remains to exemplify some of the above processes through presentation of selected known examples. Most of those so far discovered fall in the symmetry-allowed thermal s, a, a, a class. Perhaps best known is the addition of olefins to bicycloheptene (129: (288)→(289)).

Further examples in this group are the reactions (290)→(291), (292)→(293), and (294)→(295).

Further examples in this group are the reactions (296) to (301).

6.4. Prisms

To what does this fantastic molecule (296) owe its capacity to survive? Is it there stored at least one kilocalories of energy more than it contains in its bis-

What are the new orbitals thus generated? They are precisely the molecular orbitals of the benzene molecule. But while two of the bonding and antibonding orbitals of prismatic (297) and (298) have transformed into two bonding orbitals of benzene (299) and 299), the (m) becomes an antibonding orbital of the product (297). Physically, this correspondence introduces an antibonding, energy-raising component into the transformation state for the transformation. It is that component which makes the transformation of prismatic into benzene symmetry-forbidden, and permits the former to exist.

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transformation from the symmetry-allowed class to which it might formally be assigned on casual inspection. When we scrutinize the offending bonding anti-bonding correlation of the orbitals $\sigma_1$ (302) and $\sigma_2^*$ (303), we see at once that it is the development of radical anti-bonding, energy-raising relationships at the $3.6, 1.9, 2.4$, and $3.4$ bonds, necessitated by the presence of the invariant framework $\pi$ bonds in the prizmic molecule, which differentiates the prizmic - benzene transformation from the general [2+3+2] cycloaddition reaction. When, as in the last, $\pi$ bonds are absent, these antibonding, energy-raising components are also absent.

The point may be illustrated further by considering certain molecules closely related to prizmic. Consider first quinacridone (304) and the triethylenes (305).

These molecules might at first sight be expected to be susceptible of symmetry-allowed transformation to cyclooctatetraene (306) and hexatriene (307), but analysis shows that, in the case of prizmic, the presence of the framework $\pi$ bonds places the changes in the symmetry-forbidden category. It is worthy of note that, in fact, quinacridone is not converted to cyclooctatetraene, even at very high temperatures (308). In that light, the oxygen analogue (309) is of special interest. In this case, the product of a [2+2, 2+2, 2+2] cycloaddition is oxepine (309), and the orbital correlation analogous to that which leads in the other cases to an antibonding level gives now the highest occupied ground-state level, which is probably weakly bonding. It is gratifying to note that derivatives of the oxo analogue are smoothly transformed to cyclopentene when heated (122, 124).

Another relative of the prizmic molecule is the bicyclo[2.2.0]hexane (310). In this case, lacking as it does $\pi$ bonds joining C-1 to C-5, and C-2 to C-4, no offensive nodes develop at the transition state for a [2+2+2] cycloaddition, as it is thermally approached, the thermal transformation of (310) to ethylene and butadiene (311) is symmetry-allowed. In fact, it has not as yet been observed. When the unsubstituted bicyclo[2.2.0]hexane (312) itself is heated, it is converted to 1,5-hexadiene (313) and ethylene (314) - either by a two-step mechanism involving an intermediate (314), or by a symmetry-allowed [2+1+2] path.

6.2. [2+2+2+2] Cycloadditions

The [2+2+2+2] cycloaddition reaction is symmetry-allowed:

a) For ground state reactants, when an odd number of components is involved in a suprafacial manner.

b) For reactions in which one component is in an excited state, when an even number of components is involved in a suprafacial manner.

Obviously, entropy factors render polymerization reactions of this type very highly improbable. Just as obviously, this difficulty can be surmounted by the manipulation of building all the components into a single molecule, geometrically prepared for their eventual dispersal. Such examples have already been mentioned above (315 and 280).

Symmetry-allowed many-component fragmentations are also opposed by a special factor; for each $\pi$ bond which is transformed into a $\alpha$ bond an endothermicity of some twenty kilocalories must be expected.

There are instances of [2+2+2+2] cycloadditions masquerading as other processes. Consider for example (316).

7. Theory of Sigmatropic Reactions

We define as a sigmatropic change of order [3,1] the migration of an $\pi$ bond, flanked by one or more $\alpha$ electrons, to a new position whose terminus is $\pi$ and $\alpha$ atoms removed from the original bonded pair, in an unstrained intramolecular process. Thus, the well-known Claisen and Cope rearrangements are sigmatropic changes of order [3,3].

A priori, there are two topologically distinct ways of effecting a diazomethane migration. These are illustrated in Figure 28 for the [1,3] shifts of a hydrogen atom. In the first, suprafacial process, the transferred hydrogen atom is associated at all times with the same face of the $\pi$ system. In the second, antarafacial process, the migrating atom is passed from the top face of one carbon atom to the bottom face of the other.

For the analysis of these reactions correlation diagrams are not relevant since it is only the transition state and not the reaction or products which possess molecular symmetry elements. We shall nearest several equivalent methods for analyzing reactions.

1. The use of the principle of conservation of orbital symmetry is here illustrated for the case of a suprafacial...
facial [1,3] hydrogen shift. The relevant correlations are shown in Figure 29. Clearly, two electrons can enter a bonding orbital, either as a pair, or as separate electrons, but the other two must be placed either in a π* or a σ* orbital, if orbital symmetry is to be conserved. The reaction is exothermic-forbidden.

2. In the [1,3] sigmatropic migration of hydrogens within an alkoxy-polyene framework (239) (23) one may envisage the transition state as being made up by the combination of the orbital of a hydrogen atom with those of a radical containing 2π electrons. The highest occupied orbital of the framework system is the nonbonding allylic orbital which possesses the symmetry shown in (322). Consider a hydrogen atom bonding to

![Figure 31](image)

of the three-center bond. In the second case (Figure 32) the remnant orbital is symmetric and cannot interact in a similar way. The presence of the interaction typically stabilizes one level, and destabilizes the other. Now, since there are in all 2h+4 electrons to be accommodated — 2k electrons in bonding polyene levels, and

![Figure 32](image)

the terms of such systems. In order to avoid a high energy orbital in the transition state, it is required that positive overlap between the framework orbital and the migrating hydrogen orbital be maintained. The result is symmetry-allowed suprafacial migration for odd k, while the antisuprafacial path must be followed for even k.

3. Let us now examine the transition state from a different, but equivalent, viewpoint. First, we write down an explicit three-center bond involving the termini of the carbon chain and the migrating hydrogen atom. The three-center bond has the typical level pattern indicated in Figure 30. There remains a 2N−1π orbital in the system in the carbon chain. The molecular orbitals of

![Figure 30](image)

this remnant are next classified with respect to the symmetry element (two-fold axis or mirror plane) present in the transition state. There now arise two cases, differing in the symmetry of the nonbonding orbital of the remnant. In the first case (Figure 31) this orbital is antisymmetric and interacts strongly with the central orbital of the three-center bond. In the second case (Figure 32) the remnant orbital is symmetric and cannot interact in a similar way. The presence of the interaction

![Figure 33](image)

relation to both π systems through which the π bond is growing. The selection rules are summarized in Figure 33. If the above treatment of [1,3] sigmatropic changes, we have considered only those cases in which a π orbital of the migrating group interact with a π system in the transition state, and migration occurs with retention of configuration at the shifting site. When the migrating group possesses an accessible σ orbital and is not so substituted as to create an impossible steric situation in the transition state, alternative processes using that σ orbital must be considered. Clearly, such changes must proceed with inversion at the migrating center, if (329), and the selection rules are precisely reversed from those given in Figure 33.

![Figure 34](image)

A number of special points pertinent to sigmatropic changes should be noted.

a) Antarafacial processes are obviously impossible for transformations which occur within small or medium-sized rings.

b) Dissociation of the carbon framework, with consequent loss of coupling within the π system, may render a symmetry-allowed process difficult or impossible of realization; for example, this factor makes the anti-suprafacial process difficult or perhaps impossible in the [1,3] case, but is not an impediment for the [1,7] reaction.

c) A cyclopropane ring may replace a π bond in the framework system for a sigmatropic change.

d) Orbital symmetry arguments are applicable to sigmatropic changes within these species. Thus, the suprafacial [1,2] shift within a carbon 2π system is symmetry-allowed and very well known. The predicted [1,4] shift with inversion of the migrating group, within a binomen 2π system has only recently been observed. We may expect that the [1,6] shift within a hexa-2,4-dien-1-yl radical will take place through a readily accessible suprafacial transition state.

e) It remains to point out that the insights afforded by the discussions presented in the preceding sections allow you to view sigmatropic changes as cycloaddition reactions. Thus, the [1,3] sigmatropic process (329) → (330) is a [2,2→4] reaction, and the [1,3] sigmatropic rearrangement (331) → (332) is a [2,2→3] concerted cycloaddition.

![Figure 35](image)

This is derived from the fact that the first two alternatives depicted in Figure 34 are simply different ways of regarding the same physical process. Consequently, the analysis yields as it must essentially the same conclusions reached in our prior discussions of sigmatropic reactions.

3.1. Sigmatropic Reactions Examined

Few thermal unactivated [1,3] shifts are known. Those which do exist include a number of unactivated [1,3] shifts, such as the vinylketone-π-π system rearrangement, proceed with such high activation energies for 30 kcal/mole that the entropy of the activated complex cannot be calculated. These are stepwise processes. None of the Bass and Nelson (191) recently made the dramatic observation that (329) undergoes a concerted symmetry-allowed suprafacial [1,3] shift, with inversion at the migrating center (stabilized), to give (329), at 307°C. The trans (328) owes its relative stability to the requirement of a symmetry-forbidden [1,3] shift for an unactivated rearrangement to occur.


The rearrangement of the ester (331) of Est's acid is an especially interesting [1,3] sigmatropic transformation. Studies on the optically active substance have demonstrated that the reaction occurs with high stereospecificity[144]. Of the two possible symmetry-allowed skeletal processes - [1,3] suprafacial migration with inversion at the migrating atom and [1,3] antarafacial shift with retention - the latter is rendered inaccessible by the constraints imposed by the ester.

Since substituents are present, the allowed and accessible process may be realized in two electronically identical, but sterically different, ways. Consequently, we may predict that (331) must be transformed into (332) and (333); the evidence is now conclusive[144] that the two isomers actually produced are the predicted ones.

![Chemical structures and reactions](image)

We have mentioned above that the activation energy for the vinylcyclopropene-cyclopropane conversion[147,148] is ca. 30 kcal/mole[149]. The bond-breaking process in cyclopropane itself requires an activation energy of 63 kcal/mole[147]; allylic stabilization has been estimated at ca. 13 kcal/mole[148]. Consequently, if full use be made of the available allylic stabilization energy in a diradical intermediate, a two-step, non-concerted path for the conversion of vinylcyclopropane to cyclopropane is not thermodynamically unreasonable. Some preliminary studies have yielded results consistent with such a mechanism[149]. Nevertheless, in view of the recently established occurrence of symmetry-allowed concerted processes despite extraordinarily unfavorable geometric constraints, it is worth while to consider the stereochemical consequences of the possible concerted processes for the vinylcyclopropane-cyclopropane change. Consider the maximally labeled derivative (334); the symmetry-allowed reactions are:

- an antarafacial (3) shift of bond 1,2 to C-5, with retention at C-2, leading to (335);
- a suprafacial (1,3) shift of bond 1,2 to C-5, with inversion at C-2, leading to (336).

The isomer (337) cannot be produced in a symmetry-allowed process.

Photocatalytic [1,3] rearrangements, symmetry-allowed as suprafacial shifts, have been observed in a large number of cases[150].

Specific thermal [1,3] shifts have been observed in a great number of cases[151]. The simplest case of a [1,3] shift in a 1,3-pentadiene was studied by Roth and King[152]. They compared the rearrangements of (338) and (339), and observed a large kinetic isotope effect of 12.2 at 25°C, consistent with a highly symmetrical transition state in the concerted process. The activation energy of the reaction is the same in the neighborhood of 35 kcal/mole. Direct confirmation of the concerted, suprafacial character of the [1,3] sigmatropic shift of a hydrogen atom has been most elegantly provided by the same investigators[153], who demonstrated the completely stereospecific conversion of (340) into (341) and (342).

![Chemical structures and reactions](image)

Numerous sequential [1,3] shifts have been observed in cyclopropenes and cyclopropanes[154-158].

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Photocatalytic [1,3] rearrangements, symmetry-allowed as suprafacial shifts, have been observed in a large number of cases[150].

Specific thermal [1,3] shifts have been observed in a great number of cases[151].

Still another test for the possible occurrence of a thermal [1,3] shift proved negative[154]. The 3,7-dideutero-labeled cycloocta-1,3,5-triene (343), through a series of reversible [1,3] sigmatropic shifts, involving the isomeric cycloocta-1,3,5,7-tetraene, would distribute the label statistically over all ring positions. On the other hand, a sequence of [1,3] shifts would place the label in positions 3, 4, 7, and 8 only; the latter result is experimentally observed.

![Chemical structures and reactions](image)

Photochemical [1,3] shifts of as yet undetermined stereochemistry are known in open, but not in cyclic hydrocarbons[159] and in heterocyclic[160]. Berson and Williams[161] have observed a remarkable series of isomerizations of methyl-substituted cycloheptatrienes. Their results, summarized in Figure 35, are consistent with a sequence of [1,3] sigmatropic rearrangements and electron transfer. One conclusion is that the suprafacial [1,3] shifts must proceed with retention at the shifting center. This condition implies that in each such substitution on the cyclopropene ring pivot[160]. The beautiful experimental test proposed but as yet not completely by Berson and Williams[161] necessitates the preynot of an optically active compound (346). Symmetry-forbidden [1,3]

![Chemical structures and reactions](image)

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![Chemical structures and reactions](image)
shifts with inversion - the course which would have been followed were the principle of least motion determinative - would result in racemization, while the predicted shifts with retention would lead to no loss of optical activity (Table 3).

Figure 16. Schematic view of the possible rearrangement of substances on a carbon ring rotating around a constitutional axis of a series of (1,3)-symmetrical shifts, with retention (left) or inversion (right). Note that here the rearrangement has been assumed to be planar and vertical to the plane of the graph, and are not drawn.

The Cope and Claisen rearrangements, both [2,2] sigmatropic shifts, are such common reactions that we could not possibly do justice to the many examples studied. These rearrangements are allowed both in a zep-zece and an enuo-mero manner. At first sight it would seem obvious that the transition state for the latter is sterically unsuitable. Yet an enuo-enu-Cope rearrangement has been observed, Makar.

reported the stereospecific rearrangement of (347) to (348). The case provides a striking instance of the manner in which framework rearrangement may operate to make otherwise diastereomically accessible symmetrical rearrangements possible (cf. the transition state (349)).

The enantiomeric stereochemical transformation of order [1,7] has been known for some time, in the prefacile- or coecier-isomerization [64].

In cyclohexene an enantiomeric [1,7] shift is impossible. Consequently, [1,7] shifts within this system must be photochemically induced, or occur with inversion at the shifting site if thermal.

[1,2] Shifts in a carbonium ion are very common. Stereospecific proton or methyl shifts in benzene-mum cata was [170] may be regarded as [1,2] or [1,3] shifts.


Signarator reactions of order [1,4], e.g., migrations in a 1,2-bis-2,3-dionyl carbon, have not been observed until recently, when Swift and Harp reported the very rapid degenerate rearrangement (336) in short time.

A [1,4] sigmatropic shift constrained to proceed suprafacial must take place with inversion at the migrating group. Note how this prediction contrasts with that for the [1,5] shift in the sterically very similar (337).

The predicted inversion in a [1,4] sigmatropic shift has recently been verified by several groups, Hf, H, and Zimmermann [174] have demonstrated that such a process occurs in the Pfeffer reaction of a bicyclo[3.1.0]hexane (338) to (339) (360).

The occurrence of [1,4] sigmatropic rearrangements, the [1,4] sigmatropic reactions are competitive with equally allowed [1,2] and [1,3] shifts.

There also may be at hand some examples of [2,2] anionic sigmatropic reactions, in the Wittig rearrangement - the base-catalyzed transformation of enol ethers to alcohols. Thus, Makimura and Notzmann [177] observed the base-catalyzed conversion of (364) to (365). Similar results are labeled 2-fluoroallyl ethers were obtained by Schöllkopf [178]. The isoelectronic analogue (366) to (367), within formally neutral species, has been found to occur readily, and has been recognized as a very general reaction-type [179].


n even

\( 2n - 2 \leq (n - 1) + \text{some even number} \)

\( \text{Effective} \)

\( \text{Ineffective} \)

So far we have deduced the number of moves necessary to reduce the distance to 1, but if it may be at any even-numbered vertex. Now, A and B having been placed at any adjacent vertices, an even number of ineffective moves will suffice to realize the final objective of placing B at position 2, and A at position 3. We have thus shown that the total number of necessary moves is:

\( (n - 1) + \text{some even number} \)

Consequently, the required number of moves is odd if \( n \) is even, and even if \( n \) is odd, which was to be proven.

For cationic sigmatropic rearrangements, the topological relationships can differ significantly from those just shown to be general for neutral species. We consider first the sigmatropic rearrangements of bicyclo[1.1.1]pentan-2-yl cation (396). In this system (396),

\[ \text{[1,4], and [1,3] shifts may occur; experience indicates that ionic [1,2] shifts should be much faster than the neutral [1,2a]-[1] rearrangements. Using the previous conventions, and observing the symmetry-imposed conditions that [1,2] shifts occur with retention, while [1,3] and [1,4] migrations must take place with inversion, we obtain the interrelations shown in Figure 39. The relationships are summarized in (387) and (388).} \]

8. Group Transfers and Eliminations

Consider the concerted reaction in which two hydrogen atoms are transferred from ethane to ethylene (392), in a process suprafacial on both reactants. A correlation diagram (Figure 40) is easily constructed for this reaction, utilizing the symmetry plane bisecting the two molecules; the process is clearly symmetry-allowed. In contrast is the diagram (Figure 41) for the

\[ \text{[1,4]-, and [1,1]-membered rings – as well as in the three-membered case (cf. Figure 39).} \]

\[ \text{Figure 10: 11b: Sigmatropic shifts in bicyclo[1.1.1]pentan-2-yl cation.} \]

\[ \text{Figure 11: Correlation diagram for the concerted transfer of two hydrogen atoms from ethane to ethylene.} \]
conducted transfer of two hydrogen atoms from ethane to the terminal of butadiene (1981); the reaction is symmetry-forbidding.

For the general case (1984), it is simple to derive the following selection rule. The double-group transfer is symmetry-allowed for ground states when $m-n=4q$, for excited states when $m-n=4q$, where $m$ and $n$ are integers. The rule applies also to a process anarrafacal on both components, and is reversed for a process anarrafacal on one component only. The rules must be properly modified if the possibility of inversion at $R$ is real (cf. Section 11).

The best known example of this type of reaction, with $m=0$, $n=1$, is the transfer of hydrogen from ethane to olefins. 

Hydrocarbons analogous also exist; for example, the reaction (395) was observed by Donning and Rees.

1983 P. Donald. personal communication; J. Fleeming. personal communication.
1990 W. R. Baush. personal communication.

As for the concerted transfer of two hydrogen atoms from ethane to the terminal of butadiene (1981); the reaction is symmetry-forbidding.

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forces[199], electrostatic forces consequent upon charge transfer between dine and dinitrophenol[200], and mass addition accumulation of 1,2-addition[198]. In particular, it is now clear that in some cases the orbital interactions among unoccupied centers involved in a concerted cycloaddition reaction will be such as to raise rather than lower the energy of the reactant transition state, and lead to a preference for 1,3-dipole addition, instead of

symmetry factors are dominant; inspection of the relevant orbital diagrams (402 and 404) for the symmetry allowed $[2+2]$ and $[2+4]$ combinations indicates that it is such a case.

This prediction was made prior to the discovery of [6+4] cycloadditions, and has since been confirmed[201]. By contrast, the symmetry-allowed $[3+2]$ and $[2+2+2]$ combinations should sensitize the reactant process and proceed by preference through ene transition states; there is already evidence for such preference in an example of the latter process[202].

The diniteration of cyclobutadiene is a special case of much interest, considered in the light of orbital symmetry relationships. If, as seems likely, there is substantial double bond character in that highly reactive molecule, one can delineate, a priori, the possibilities of $[3+2]$, $[2+2+2]$, and $[2+2+2]$ cycloadditions. Our selection rules require a preference for the concerted $[2+2+2]$ process, and indeed evidence of this path has been brought forward[200]. Examination

likelihood of the transitory existence of a free cyclobuta
diene, the predicted ene process was observed[200].

The $[3+2]$ sigmatropic shift in 1,5-enediones has been shown to proceed more easily through a four-center

chair-like transition state (407) than through the boat-like alternative (408) [203]. We suggest that orbital symmetry relationships may play a major role in determining that preference. A correlation diagram for the mol
ecular orbitals involved in the rearrangement is illustrated in Figure 42. The levels are classified as symmetric or antisymmetric with respect to the mirror plane $m$ in the boat-like transition state, or a two-fold rotation axis in the chair-like form. The scheme shown is for the former case, and the diagram for the latter is qualitatively similar. The correlation of reactant bonding levels with product bonding levels, characterized by a symmety-allowed thermal reaction, should be noted.

At the half-way mark in the reaction the level ordering is recognizable as that of two strongly interacting alkyl radicals. The actual behavior of the levels along the

in the other a quasi chair fashion. In each of these processes there are two symmetry elements:

1) in a boat, both a mirror plane $m$, which passes through C-2 and C-5, and bisects the angles C(1)-C(2)-C(3) and C(6)-C(7)-C(8); 2) in the boat approach, a second mirror plane, $m_{1}$, parallel to and half-way between the planes of the approach radicals, and in the chair approach a two-fold axis of symmetry, lying on the intersection of $m_{2}$ and the plane defined by C(1)-C(3)-C(4)-C(6).

To complete the correlations one must specify the end products of these hypothetical motions; these are a bicyclo[2.2.0]hexane in the boat approach, and a 1.4-cyclohex
dienone in the chair approach. Among the occupied levels the critical differences in the two pathways is in the behavior of the occupied $S_{A}$ level, which in the boat-like approach correlates to an antibonding $S_{A}$ orbital, while in the chair-like process it goes over to a non-bonding biradical level. The crucial point of the argument now is a reaction proceeding as in Figure 42 must pass at the half-way point through some point in a correlation diagram resembling one or the other of those shown in Figure 43, and that this point will be approximately the same horizontal distance, marked by dashed vertical lines, along the reaction coordinate in the two alternate pathways of Figure 43. Further, at any such point the chair-like transition state is at lower energy as a result of the difference in correlation properties of the occupied $S_{A}$ orbital. The central conclusion is that orbital interactions involving C-2 and C-5 have a net antibonding, energy-raising effect. In this sense, the argument represents a further development of the simple orbital repulsion effect suggested by Doering and Berry[201].

It should be emphasized that the effects discussed here are, not unexpectedly, small ones, and that in systems possessing special geometrical requisites which necessitate a boat-like transition state[201], significant changes take place with no special difficulty[204].

To present a final illustration of the procedure, in a case in which the result is not yet known, we consider the $[4+2]$ cycloaddition of a butadiene to an alkyl cat

in that sense the reaction coordinate resembles one or the other of those shown in Figure 43, and that this point will be approximately the same horizontal distance, marked by dashed vertical lines, along the reaction coordinate in the two alternate pathways of Figure 43. Further, at any such point the chair-like transition state is at lower energy as a result of the difference in correlation properties of the occupied $S_{A}$ orbital. The central conclusion is that orbital interactions involving C-2 and C-5 have a net antibonding, energy-raising effect. In this sense, the argument represents a further development of the simple orbital repulsion effect suggested by Doering and Berry [201].

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10. Divertorment!

In the previous sections, we have discussed and exemplified orbital symmetry control of the major general types of concerted organic reactions. We turn now to a discussion of two special types, each of which possesses fascinating unique features, and further illustrates the power of the principle of orbital symmetry conservation in understanding and predicting the detailed course of chemical transformations.

10.1. Chelotropic Reactions

We define as chelotropic reactions those processes in which two π bonds which terminate at a single atom are made, or broken, in concert.

Let us consider: the chelotropic reaction (411), in which a small molecule X(YZ) is added to a polyene containing an n-electron π system (figure 410). We shall examine the geometrical aspects of the reaction, with reference to an invariant coordinate system (412), whose origin is always at X, and whose z axis bisects the line between C1 and Cm. Thus, the π bonds being broken lie in the yz plane, and their four electrons are distributed as usual, in pairs, in the two generalized orbitals (413) and (414). Now, in general, two electrons must be delivered from these orbitals to each of the developing products, with conservation of orbital symmetry. A crucial point now emerges: the transfer of two electrons from the breaking π bonds to new orbitals in the product molecule X(YZ) may take place in either of two sharply different ways.

a) Two electrons from the symmetric orbital (415) may take up new positions in a z-symmetric lone pair orbital of X(YZ), or enter an α system antisymmetric with respect to the xy plane.

b) Two electrons from the antisymmetric orbital (416) may take up new positions in an x-symmetric lone pair orbital of X(YZ), or enter an α system antisymmetric with respect to the yz plane.

In the light of this analysis, it is clear that the geometrical displacements at C1 and Cm are dependent upon the detailed geometry of departure of X(YZ), and in particular, on the sense of the displacements of the atoms YZ ... which are attached to X. To illustrate this important point, we consider the departure of a bent molecule Y-X-Z, which as it develops must acquire a symmetric lone pair at the central atom X. The reaction may take place in either of two ways, depicted in (417) and (418).

Figure 44. Selection rules for chelotropic reactions.

The selection rules are summarized in Figure 44. In these chelotropic transformations there undoubtedly exist, for each ground state reaction, an excited state process characterized by reversed stereoechemical features. However, the extruded small molecule X(YZ) will frequently possess many occupied lone pairs orbitals, and the accompanying possibility of numerous n-n* states raises the possibility in any given case that excited state processes will be of the same stereoechemical characteristics as the corresponding ground state transformation may be available.

Linear chelotropic fragmentations leading to the production of nitrogen or carbon monoxide represent reactions well-suited for the construction of formal correlation diagrams, which have been drawn by Lehn (1970), and by Baldwin (1980), as well as by us. For car-
but monoxide elimination no direct stereochemical results are available. It is clear, however, that cyclopentene-1,2-dione (m-4) undergo deacylation readily, as demonstrated previously [24]. In this connection, the failure of attempts to prepare norbornadiene (25) may be contrasted with the stability of the norbornenes [20].

![Image](image_url)

A case with m-6 is represented by 3,5-cyclooctadiene (27), which in one of the few known condensation-dicarboxylation, undergone photo sensitization and carbon monoxide (28).

![Image](image_url)

The elimination of nitrogen from diazines (28) has been carefully studied by Lemel [20]. The process is stereospecific and disrotatory, as predicted: the linear disrotatory path is clearly one involving less strain than the non-linear disrotatory alternative in this case.

![Image](image_url)

Remarkable sequences (247), (248) comprising disrotatory nitrogen eliminations, followed by cyclizations (249) have been revealed by Clar [21].

![Image](image_url)

The reversible, facile addition of sulfur dioxide (250) to dienes is well known [22]. The expected disrotatory

![Image](image_url)

course for the elimination of sulfur dioxide from a bicyclic sulfone has been established [23]. The corresponding photochemical process is not completely stereospecific, but a clear preference for the disrotatory path is shown [24]. Sulfur dioxide also readily undergoes 1,6-addition to 2,3-benzisoxazole; the stereochemistry has been demonstrated to proceed in a disrotatory fashion, and must therefore be classified as a linear reaction [25].

![Image](image_url)

Chelotropic reactions in which a three-membered ring is produced or destroyed, e.g., fragmentation of type (251) in which m-2, are of special interest in that geometric factors require that they take place in a disrotatory, or suprafacial manner. Consequently, these transformations must occur by the non-linear chelotropic path.

![Image](image_url)

The well-known stereospecific combination of single carbones with olefins to give cyclopropanes unambiguously falls in the non-linear chelotropic class [26].

![Image](image_url)

Cyclopropanes and cyclopropenes lose carbon monoxide thermally under mild conditions [27,28], and even more readily on irradiation [29,30]. Stereochemical information on the deacylation is lacking. It has, however, been clearly demonstrated that nitrogen is stereospecifically extruded in a disrotatory fashion from alkyl-substituted three-membered rings.

![Image](image_url)

Available evidence is also consistent with the view that the elimination follows the concerted symmetry-allowed non-linear chelotropic path [cf. (480)].

![Image](image_url)

The observed ready elimination of nitrous oxide [21] from N-nitrosoamines [22] probably also follows the non-linear chelotropic path [42]; it is unlikely that the molecule will make use of this alternative symmetry-allowed process to destroy itself.

![Image](image_url)

The hypothetical abstraction reaction (485) provides a further example of a chelotropic change. If the abstraction takes place in a linear fashion, the lone pair of the amine and the two oxygen lone pairs are transformed into the NO bond and the 1π and 3π unpaired pairs of the NOxide (487). The remaining 2π axole lone pair of the NOxide must be taken from the antisymmetric orbital of the breaking carbon-oxygen bonds. Therefore, two electrons from the corresponding symmetric orbital must be delivered to the polyene product.

![Image](image_url)

[20] J. F. Ferranti and W. H. Gisham, J. Amer. chem. Soc. 82, 3086 (1961). However, the corresponding ortho-substituted case (423) is a non-stereospecific process (personal communication from L. A. Carper).


Consequently, the reaction must occur in a disrotatory sense when \( n > 4 \); or, conversely, when \( n < 4 \). If, on the other hand, the amine attacks in a non-linear manner, i.e., in the xy plane, but in the z-direction, the stereochemical consequences are precisely reversed. A possible analogue of the linear reaction is available in the stereospecific abstraction of sulfur from the cis- and trans-butene sulfinylides by phosphines [227].

A fascinating combination of a chelotropic fragmentation with a vicinal elimination is presented by the decomposition of a spirocyclic to char dioxide and olefins. As yet, the only known instance of the reaction involves ethylene ketones derived from substituted 2-norbornadienones [438](228). It is most interesting to examine the stereochemical aspects of the process in the general case [443]; \( m \) and \( n \) represent the numbers of electrons in the \( n \) systems of the product polyenes. In addition to the four electrons which constitute the skeletal \( \pi \) bonds, carbon dioxide (440) requires twelve electrons: six of these populate two perpendicular 4\( \pi \) systems, in the \( yz \) and \( zx \) planes, respectively, while four occupy two \( \pi \)-symmetric lone pair orbitals. If the reaction under discussion follows the linear chelotropic path, it is clear that the eight lone pair electrons at the oxygen atoms of (449) pass unimediately into the \( \pi \)-symmetric lone pair orbitals and the 4\( \pi \) system of carbon dioxide (440), with conservation of orbital symmetry. Further, the orbitals of the orthogonal 4\( \pi \) system can only be filled by transferring two electrons from the symmetric C–C–O orbital (441) to the lowest occupied \( \pi \)-symmetric C–O orbital (442), and two from the antisymmetric C–C–O orbital (444) to the highest occupied \( \pi \)-symmetric orbital (443). Therefore, the electrons occupying the antisymmetric C–C–C–O orbital (446) must be delivered to the highest occupied orbital of the polyene (445), while those in the symmetric C–C–O–O orbital (447) take up their new positions in the highest occupied orbital of the polyene (448). Consequently, the geometric displacements associated with the carbon-carbon bond cleavages will be disrotatory when \( m < 4 \), or non-linear when \( m > 4 \); by contrast, the carbon-oxygen reactions will be associated with disrotatory displacements when \( n < 4 \) or \( n > 4 \). If the reaction follows the non-linear chelotropic path, the stereochemical consequences attendant upon the carbon-carbon bond cleavages will be reversed. Finally, it may be noted that if there is a minimum in the potential surface for the reaction, representing the intermediacy of a single seven-membered species (443), the analysis in terms of orbital symmetry conservation is unchanged.

It might appear that in respect to chelotropic reactions, the principle of orbital symmetry conservation is rather generous than discriminative. But that is not so. Chelotropic reactions are unusual in that the stereochemical inferences imposed by orbital symmetry control upon one of the reactant sites leave no imprint upon the products. Consequently, verification of the predictions which can be made on the detailed course of chelotropic reactions cannot be achieved simply by examining the stereochemistry of the products, and awaits more sophisticated scrutiny.  

10.2. Cycloaddition Reactions of Ketenes

The combination of ketenes with olefins to give cyclobutanes has long been known [129]. In recent years, the reaction has been subjected to very searching scrutiny, and the evidence is now conclusive that it is concerted. Thus, the reaction proceeds with a high negative entropy of activation [130] (the dependence of rate on solvent polarity is modest [129, 221], and stereochemical relations in the reactants are maintained in the products [131]). The most striking instance being the formation of disulfane adducts from the reactions of dichloroketene with the cis- and trans-cyclooctynes [132]. Most compelling is the observation that the reaction of ketenes with diamines—especially those containing disulfane—gives only cyclobutanes, and no cycloheptenes [124]. For example, cyclopropenide and diphenylketene react to give (450); so (451) is produced.

\[ \text{the vinylion ions (green in (453) and checkered in (456))} \]

It is at once apparent that the latter special feature contributes two strong bonding interactions (dotted lines in (453)) which are absent from the (2+1) reaction path for complexation. It should be noted that what is presented is such that the tops of the vacant \( p \) orbitals are seen, and that it is the bottom of that orbital which is bonding to the occupied system of the simple dianion reactant (cf. [453]). To put the matter in another way, the normal symmetry-allowed combination of cation with an ethylene, in this unique situation sets the stage for and is consonant with the (2+2) cyclodaddition reaction.

In the light of the analysis just presented, it is clear that a vinylion ion must be regarded as a constitutional exode of excellent performance for participation as the (2+2) component in the most capable of the 

\[ \text{\text{[453]}}, \text{\text{\text{[454]}}} \]

But, for the ketene, the ketene orbitals are not significantly more complexed than the 

\[ \text{\text{[453]}}, \text{\text{\text{[454]}}} \]

It is clear that the analysis is consonant with the vinylion ion, but that the vinylion ion possesses in high degree the predicted capacity for concerted combination with the \( p \) system.

And now we can answer emphatically in the affirmative the question which launched the discussion just concluded. Ketenes, in their capacity as vinylion ylides (453), are in fact ideally constructed to play an antafacial role in reaction with \( p \) systems, and it is that symmetry-allowed role which they exhibit in the many observed concerted combinations with olefinic systems. Of course, ketenes are not simple vinylion ions, but pair at oxygen: expected to have a major effect. Thus, in participating in cycloaddition reactions as \( p \) components, ketenes should not differ markedly from normal alkyl ylides. Consequently, in the reactions of ketenes with dienes, the symmetry-allowed \( \text{[451]} \) reaction is not expected to be a ready one. Further, the \( \text{[451]} \) reaction is of course symmetry-forbidden, and the presence of an orthogonal vacant \( p \) orbital, or low-lying \( p \) system, cannot facilitate the \( \text{[451]} \) process. Taken together, these circumstances account for the formation of cycloadducts to the exclusion of cyclohexadiene when ketenes react with simple dienes.

11. Generalized Selection Rules for Pericyclic Reactions

In our development of the theme of orbital symmetry control of concerted chemical changes, we have laid the basis for a general consideration of all pericyclic reactions - that is, reactions in which all first-order changes in bonding relationships take place in concert on a closed curve. Thus, we have discussed in detail the orbital character of various clearly definable reaction types. But we have also made it clear that the different classes have much in common. In particular, we have pointed out that electron-deficient reactions and singlet electronic changes can as well be treated as concerted intramolecular cyclization processes. Now, we develop further the generalization that all pericyclic reactions may be categorized into concerted cyclization processes, and must obey the selection rules for such changes.

The selection rules for two-component cyclizations (cf. Figure 22, Section 6) may easily be generalized by reduction to include any number of components. In that way we derive the following general rule for all pericyclic changes:

\[ \text{\text{[462]}} \]

\[ \text{\text{[463]}} \]

\[ \text{\text{[464]}} \]

\[ \text{\text{[465]}} \]

\[ \text{\text{[466]}} \]

\[ \text{\text{[467]}} \]

\[ \text{\text{[468]}} \]
The [2,1] sigmatropic shift within a cation cannot take place with inversion of the migrating group, since the $[3\beta-\alpha\beta\gamma\delta]_{(465)}$ and $[\alpha\beta\gamma\delta-\alpha\beta\gamma\delta]_{(466)}$ processes are symmetry-forbidden. Note that antiarafacial bonding.

\[ [\alpha\beta\gamma\delta-\alpha\beta\gamma\delta] \]

Interaction between two atoms joined by a non-participating bond and bridged by a single atom is physically impossible. Thus, the $[\alpha\beta\gamma\delta-\alpha\beta\gamma\delta]$ and $[\alpha\beta\gamma\delta-\alpha\beta\gamma\delta]$ both represent the symmetry-allowed, but physically unrealizable aantarafacial [2,1] sigmatropic shift with inversion at the migrating center.

The example is included partly in a sporting spirit, but it does have the serious purposes of indicating that (i) the participation of any number and kind of co-components in a pericyclic reaction presents no occasion for difficulty in analyzing the process in terms of the general rule, and (ii) polarization of the bonds involved in a pericyclic reaction in no way alters the orbital symmetry control to which it is subject.

It should be emphasized that use of the general selection rule for pericyclic reactions must always be subject to the following precautions:

a) The geometry of each individual case must be examined on its merits in order to ascertain whether the process is physically realizable. We have already exemplified, in (d) above, and in our discussion of the rearrangement of the ester of Pfeff’s acid [cf. (473)], Section 7.1, situations in which formally symmetry-allowed processes are geometrically impossible.

b) In cases in which the reacting components are directly joined by non-participating bonds, forced auxiliary off-cycle antibonding interactions may render an otherwise allowed reaction symmetry-forbidden. Thus, for example, the $\text{[2\beta\alpha\delta-\alpha\beta\gamma\delta]}$ process. The geometric constraints imposed by the non-participating $\alpha$ framework require that the ethylene moieties produced in such a reaction interact strongly in an antibonding way, and the orbital symmetry-imposed electronic configuration of the array is in fact that of a doubly excited state of the actual product benzene [cf. Section 6.4]. Any case in which similar circumstances may be suspected should be subjected individually to complete analysis, in the light of the principle of orbital symmetry conservation.

12. Violations

There are none!

Nor can violations be expected of so fundamental a principle of maximum bonding. All the more is it then important to give consideration to some reactions which might appear on casual inspection to contravene orbital symmetry conservation.

First, it should be emphasized explicitly here that a given symmetry-allowed concerted reaction need not necessarily represent the manner in which reacting molecules actually comport themselves. Quite possibly another path, involving reactive intermediates of relatively low energy may be other. The other side of this coin is that molecules may in some cases combine, or decompose, to give the very products which would result from symmetry-forbidden concerted processes. In these cases it is clear that the actual reaction path is a non-concerted one, involving discrete intermediates; indeed, the principle of orbital symmetry conservation is of very useful in defining conditions in which such processes may be expected. Such are often the circumstances in the combination of ethylene to give cyclooctatetraene, the direct, concerted $[2\alpha\beta\gamma\delta-\alpha\beta\gamma\delta]$ formations of course symmetry-forbidden, and the allowed $[\alpha\beta\gamma\delta-\alpha\beta\gamma\delta]$ reaction is realizable only in special circumstances. Nevertheless, there are at least two distinct intermediates, leading, the special requisites for the $[\alpha\beta\gamma\delta-\alpha\beta\gamma\delta]$ reaction, in which the combination of two ethylene molecules leads to a cyclooctatetraene. [42]. And in fact, once available, the compelling in favor of the view that discrete diatomic or ionic intermediates are involved [42]; further, it is of obvious significance that such reactions are observed only when the reacting olefins are saturated by substituents so constituted as to provide effective stabilization of the requisite intermediate.

It remains only to address a few final comments to the matter of symmetry-forbidden reactions which may occur in a concerted fashion, in principle, of course, given sufficient energy, and means of constraining molecules in energy-rich configurations, we could bring about any symmetry-forbidden reaction. A very powerful means of doing this would be by grasping a molecule of ethylene in each hand, and - not without an impressive exhibition of his strength - forcing the two together face-to-face. He could then make a molecule of cyclooctatetraene at his whim, and may even wish to see it open in a diastereotopic fashion to obtain butadiene. But without such demonstrative intervention, molecules will very rarely comport themselves in like fashion - since reaction paths with lower energy surfaces than those associated with symmetry-forbidden processes will almost always be available. None the less, the possibility remains that molecules may be constructed within which no other such alternatives exist; then, provided that the molecule is sufficiently energized, the symmetry-forbidden path would necessarily be followed. Derivatives of cyclooctatetraene [42] probably exemplify such a process. These substances do undergo conversion to the corresponding benzene, with an activation energy in the neighborhood of 37 kcal/mole [42]. The simple disrotatory cleavage of the central bond is symmetry-forbidden, but [42] is already strained to the extent of ca. sixty kilocalories relative to benzene [42], and the addition of a further thirty-seven kilocalories may sufficiently energize the molecule as to overcome the prohibition against disrotatory cleavage. But even in this case, the possibility is not entirely excluded that processes may take another course, and that the transformation may proceed through a discrete intermediate. For example, if the breaking of the central bond of [42] is accompanied by a quasi-stationary skewing distortion [cf. (478)]: boat-boat transformation — the result (479) is an array containing two skew allyl radical systems (C3/C5-C5-C7 and C3-C3-C5-C7), joined orthogonally at their termini. Were all bonding between C3-C5 to be lost concurrently with these

\[ [478] \]
\[ [479] \]
to completion by appropriate symmetry-allowed combinations of the isolated allyl radicals. Even if some 1,4 bonding is retained - and of course, that was the case, some 2,3 bonding would be generated - the corresponding symmetry-derived antibonding components in the transition state (7b) would be smaller than those in the transition state for the simple symmetry-forbidden thermolysis channel; it is of special interest that if (7b) should represent the transition state for the conversion of cyclopropylketones to aromatic compounds, the former should be susceptible of isomerization in the sense (400) to (411) to (412).

Finally, emphasis the fact that cis-cyclohexane-2,3-diones owe their remarkable durability to symmetry-imposed barriers, and, to introduce a light note, suggest that our fellow chemists estimate how long the isomer (412) - put together, perhaps, by our vivid" demon would survive.

13. Other Theoretical Work

In view of the fact that the principle of conservation of orbital symmetry has been found to be an exceptionally powerful predictive and interpretive tool, it is not surprising that a number of alternative theoretical approaches have been set forth. In all cases the partial conclusions, of necessity, agree in all respects with our own. Reference should be made to the interesting contributions of Fukui[33], Salem[34], Zimmernann[245], Dewar[146], Kosterhoff and von der Lage[147], and, of course, Langer-Higgins and Abrahamsson[248]. It is also appropriate here to mention some earlier studies relevant to and antecedent to our own. Correlation diagrams for the simplest chemical reactions are


Classification of Partition Reactions of Inorganic Cations

By H. Specker and A. Kettrup

In partition reactions of inorganic cations, it is necessary to establish the composition of the extracted compounds. The methods used and the limits of this application are described and illustrated for the extraction of cobalt thiocyanate. The results obtained allow new analytical applications, e.g. the fractional extraction of Hg, Bi, Cd, In, and Zn.

2. Methods of Determining the Compositions of Extracted Compounds

All the methods described below were originally developed for determination of the compositions of complexes in single-phase, particularly aqueous systems. The question of primary interest is that of the number of ligands (e.g. halide ions) bound per central atom. In extractions with solvents that are capable of coordination, we also wish to know the number of solvent molecules bound. If a definite compound, e.g. a halogenometallate 

\[ [\text{M}X_n]^m \] 

is extracted over a wide concentration range, two series of measurements with suitable variations are generally sufficient to give the numbers of halide and solvent ligands. The photometrically determined extinction value is often used as a measure of the concentration of the complex formed in solution equilibration;

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