The Conservation of Orbital Symmetry

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Orbital symmetry controls in an easily discernible manner the feasibility and stereochemical consequences of every concerted reaction.

Chemistry remains an experimental science. The theory of chemical bonding leaves much to be desired. Yet, the past 20 years have been marked by a fruitful symbiosis of organic chemistry and molecular orbital theory. Of necessity this has been a marriage of poor theory with good experiment. Tentative conclusions have been arrived at on the basis of theories which were such a patchwork on approximations that they appeared to have no right to work; yet, in the hands of clever experimentalists, these ideas were transformed into novel molecules with unusual properties. In the same way, by utilizing the most simple but fundamental concepts of molecular orbital theory we have in the past 3 years been able to rationalize and predict the stereochemical course of virtually every concerted organic reaction.[1]

In our work we have relied on the most basic ideas of molecular orbital theory—the concepts of symmetry, overlap, interaction, bonding, and the nodal structure of wave functions. The lack of numbers in our discussion is not a weakness—it is its greatest strength. Precise numerical values would have to result from some specific sequence of approximations. But an argument from first principles or symmetry, of necessity qualitative, is in fact much stronger than the deceptively authoritative numerical result. For, if the simple argument is true, then *any* approximate method, as well as the now inaccessible exact solution, must obey it.

The simplest description of the electronic structure of a stable molecule is that it is characterized by a finite band of doubly occupied electronic levels, called bonding orbitals, separated by a gap from a corresponding band of unoccupied, antiboding levels as well as a continuum of higher levels. The magnitude of the gap may range from 40 kcal/mole for highly delocalized, large aromatic systems to 250 kcal/mole for saturated hydrocarbons. It should be noted in context that so-called nonbonding electrons of heteroatoms are in fact bonding.

Consider a simple reaction of two molecules to give a third species, proceeding in a nonconcerted manner through a diradical intermediate I.

$$A + B \rightarrow [I] \rightarrow C$$

The electronic structure of diradicals is also very characteristic. In the gap between bonding and antibonding levels there now appear two nonbonding orbitals, usually separated by a small energy. Two electrons are to be accommodated in these levels, and it is an interesting and delicate balance of factors which determines the spin multiplicity (singlet or triplet) of the diradical ground state. Consider now the transformation of A + B into the singlet diradical I in a thermal process. It is easy to convince oneself that one of the two nonbonding orbitals of I arises from some bonding orbital of A or B and that the other nonbonding orbital comes from some antibonding A or B orbital. Thus, if A + B have N bonding orbitals and M antibonding orbitals than the diradical I will have $N - 1$ bonding, 2 nonbonding, and $M - 1$ antibonding orbitals. The net result in the transformation $A + B \rightarrow I$ is that one doubly occupied bonding orbital becomes nonbonding. The energy price that the molecule has to pay for this depends on the stability of the bonding orbital involved, but it is clear that the process must be endothermic. If this were the only way in which a reaction could be effected, then the price of a high activation energy would have to be paid. But in fact we have discovered that the characteristic of concerted processes is that in certain well-defined circumstances it is possible to transform continuously the molecular orbitals of reactants (say A + B) into those of the product (C) in such a way as to preserve the bonding character of all occupied molecular orbitals at all stages of the reaction. We have designated these concerted reactions as *symmetry allowed*. If there is such a pathway, then no level moves to high energy in the transition state for the concerted reaction and a relatively low activation energy is assured.

In order to establish whether a *symmetry-allowed* process is possible in any given case the safest procedure is to begin with the participating orbitals of reactants or products, allow them to interact as the reaction proceeds, and follow them through the transition state for the reaction. When symmetry of the proper kind is present this process can be made elementary by the construction of a correlation diagram. When symmetry is absent the levels can nevertheless be followed through the reaction by making use of simple quantum mechanical principles. In either case it will emerge that the highest occupied molecular orbital and its

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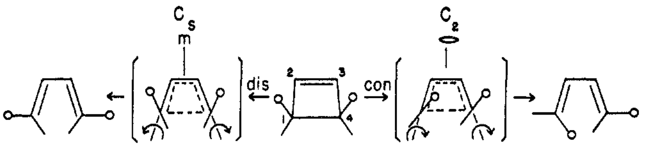
[1] R. B. Woodward and R. Hoffmann, *J. Am. Chem. Soc.*, **87**, 395, 2511 (1965); R. Hoffmann and R. B. Woodward, *ibid.*, **87**, 2046, 4388, 4389 (1965); R. B. Woodward and R. Hoffmann, to be published.

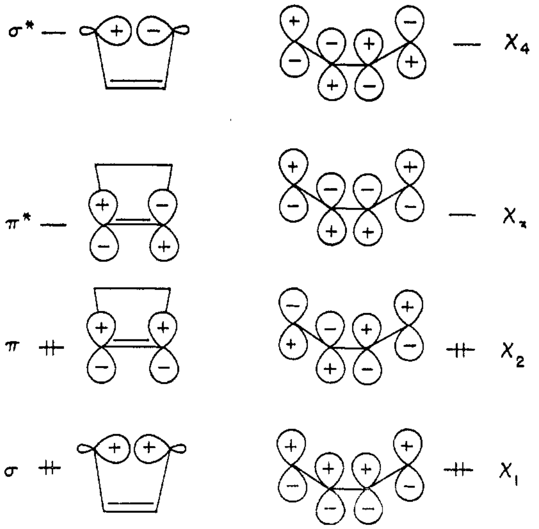
initial proclivity to rise or fall in energy along the reaction coordinate determine the course of the reaction.

To illustrate our method at work, consider the two possible modes of converting a cyclobutene into a butadiene: the motions we have defined as conrotatory and disrotatory.

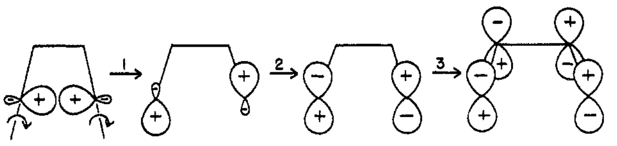


The essential molecular orbitals are the four π orbitals of the butadiene, χ_1, χ_2, χ_3, χ_4, the π and π^* levels of the cyclobutene double bond, and the σ and σ^* orbitals of the single bond to be broken.

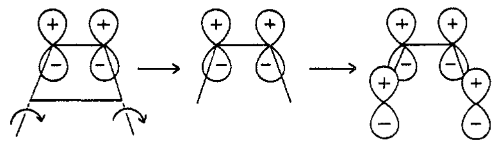
They are illustrated as



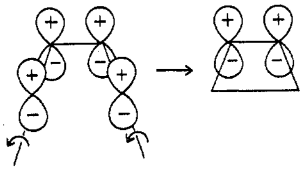
Consider carrying out a conrotatory motion to completion on σ (1) and follow through with a rehybridization (2). At this stage the orbital looks like a fragment of



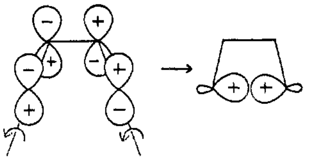
χ_2 (or χ_4) of butadiene and all that is needed is a "growing-in" (3) of orbitals at C_2 and C_3. It should be kept in mind that in reality steps 1, 2, and 3 will all be simultaneously proceeding along the reaction coordinate and the above factorization is only an aid to visualization. The "growing-in" of step 3 may seem like magic to those unfamiliar with molecular orbital calculations. It is in fact a universal phenomenon, the detailed result in this case of mixing of π^* with σ as the reaction proceeds. A general quantum mechanical result is that, if two orbitals of initially unlike energy interact, the lower orbital of the two mixes into itself the upper one in a bonding way while the upper orbital mixes into itself the lower one in an antibonding way. Thus σ is transformed in the course of the reaction into a combination $\sigma + \pi^*$ which finally emerges as χ_2, while π^* is transformed into $\pi^* - \sigma$ which concludes as χ_4. We have now followed σ through the reaction and correlated it with another bonding orbital χ_2. Similarly we follow π through. Here the "growing-in" step



is really a mixing with σ^*. π thus correlates with χ_1. The correlations could of course have been obtained starting from butadiene; χ_1 by a conrotatory motion winds up as π

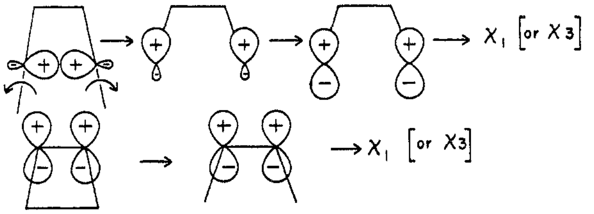


and χ_2 as σ.

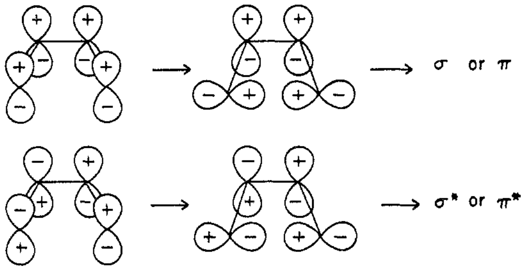


Now there appears a "fading-away" phenomenon in which extra nodes and contributions disappear. This is the precise reverse of the "growing-in" noted above and is a result of mixing with higher orbitals of the proper symmetry. Very similar arguments lead to a correlation of σ^* and χ_3 and π^* and χ_4. We have thus achieved a correlation of bonding levels of reactants with bonding levels of product, with conservation of orbital symmetry. The reaction should be thermally a facile one.

By contrast, consider now a disrotatory opening. The correlations are indicated below.

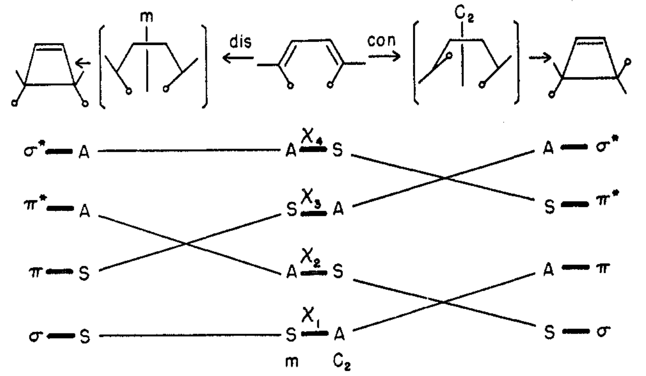


σ and π must correlate with χ_1 and χ_3. It is clear that both cannot correlate with χ_1 and so while one (say σ) does correlate with χ_1, the other must go up to χ_3, which is antibonding. Conservation of orbital symmetry requires in this case a high-lying transition state, and the thermal reaction should be difficult. Again the problem could have been approached from the other side.



It is obvious that χ_2 is the troublesome orbital—it cannot transform into *any* bonding orbital of the cyclobutene, with conservation of orbital symmetry, in a disrotatory process.

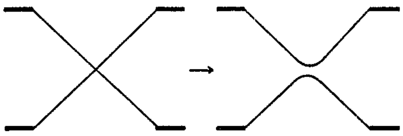
What we have somewhat laboriously described in words is the construction of a level correlation diagram. This was first done by Longuet-Higgins and Abrahamson and is illustrated below.



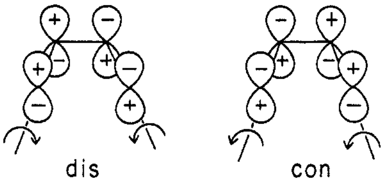
It is clear that in a conrotatory process a twofold rotation axis is maintained at all times whereas in the disrotatory motion only a plane of symmetry remains. These symmetry elements form the basis for the construction of a level correlation diagram from which a state diagram may be developed. The left of the diagram is characteristic of a thermally forbidden reaction.

The construction of correlation diagrams is simple, but there are a number of precautions and limitations one must be aware of. First, it is important to reduce the problem to isolated elementary processes or one can be misled into identifying a combination of two forbidden reactions as an allowed one. Second, a symmetry element with respect to which *all* levels have the same symmetry property is useless in deciding whether a reaction is allowed or not. Third, a symmetry element which does not pass through bonds made or broken in the reaction is similarly of no use as a guide.

Correlation diagrams represent a simple and elegant procedure when symmetry is present, but they are of little use when there is no symmetry (*e.g.*, the Alder "ene" synthesis), and mechanical construction of them can lead to serious difficulties. The primary source of trouble is the fact that symmetry is of a discontinuous nature, but chemistry is not. Thus substitution of a single methyl group at the 2 position of butadiene (isoprene) removes all nontrivial symmetry from both con- and disrotatory transition states. If one blindly drew the correlation diagram one might be led to the conclusion that since χ_2 and π are of the same symmetry they could correlate with each other in a disrotatory motion and thus make that process allowed. What happens in reality is that the loss of symmetry prevents the crossing in the level diagram, but in fact the reaction does not in the least become less "forbidden." There are still high-energy orbitals in the transition state, and it is this which is decisive. In other words, an intended crossing is just as good (or bad) as a real one. The detailed examination of levels throughout a reaction avoids the dangers mentioned above and provides a deeper physical understanding of the rationale of orbital reorganization.



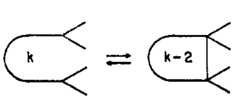
The all-important role of the highest occupied orbitals is easy to justify. First, we think of these as containing the valence electrons of the molecule, most easily perturbed during incipient reaction. In this sense their role has been stressed in the important work of Fukui and collaborators. Second, if there is little symmetry in a molecule and if there is a bonding level which is intending to cross the energy gap to correlate to an antibonding level, then that bonding level will usually be the highest occupied level. Its motion determines the course of the whole correlation diagram and its initial slope is an important indication of whether the process is symmetry allowed or forbidden. Consider the disrotatory and conrotatory motions on χ_2 in butadiene.



The disrotatory process pushes a plus lobe unto a minus. Since one end of the molecule "feels" the phase of the wave function at the other end, this is an antibonding, destabilizing, repulsive interaction. The level moves up in energy along the reaction coordinate. Conrotatory motion brings a plus lobe unto a plus lobe (or minus on minus, which is just as good). This is a bonding, stabilizing, attractive interaction terminating in the actual formation of the new σ bond.

We turn now to the presentation of some specific conclusions, illustrative of the applications of the general theory.[2] For reasons of space we wish to be excused for omitting a discussion of most of the great body of experimental facts relevant to our conclusions.

Electrocyclic Reactions. This unique class of intramolecular cycloadditions is defined by the formation of a single bond between the termini of a linear system containing k π electrons, or the converse process. 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



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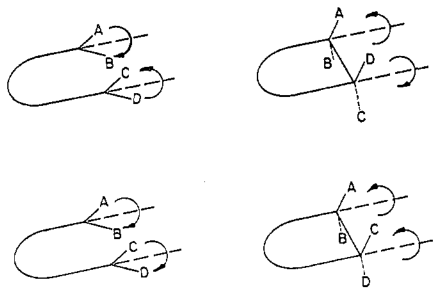
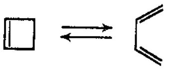
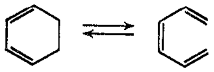
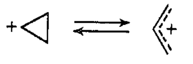
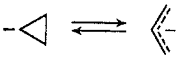
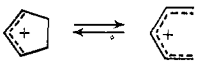
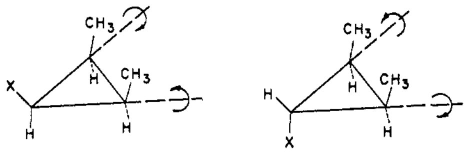
[2] These problems have been treated theoretically by others as well. See H. C. Longuet-Higgins and E. W. Abrahamson, *J. Am. Chem. Soc.*, **87**, 2045 (1965); K. Fukui, *Tetrahedron Letters*, 2009 (1965); *Bull. Chem. Soc. Japan*, **39**, 498 (1966); K. Fukui and H. Fujimoto, *ibid.*, **39**, 2116 (1966); H. E. Zimmerman, *J. Am. Chem. Soc.*, **88**, 1564, 1566 (1966); M. J. S. Dewar, *Tetrahedron Suppl.*, **8**, 75 (1967); L. Salem, *J. Am. Chem. Soc.*, in press.

relationship might be disrotatory or conrotatory; in the former case the transition state is characterized by a plane of symmetry while in the latter a twofold axis of symmetry is preserved. The electrocyclic reactions of a k π-electron system should be thermally disrotatory for $k = 4q + 2$, conrotatory for $k = 4q$, $q = 0, 1, 2, \ldots$. In the first excited state this relationship is reversed. Some specific consequences are summarized below.



	Δ	hν
	con	dis
	dis	con
	dis	con
	con	dis
	con	dis

Since there is evidence that the departure of a leaving group to form a cyclopropyl cation is concerted with the electrocyclic opening to allyl cation, there arises the possibility of discriminating among two possible disrotatory modes. This problem, posed to us by C. H. DePuy, has a most interesting solution, summarized in the illustration.



Cycloadditions. The simple terminal cycloaddition of an m π-electron system to an n π-electron molecule can proceed in four stereochemically distinct ways, illustrated in Figure 1. *trans–trans* and *cis–trans* cycloadditions appear sterically difficult and have been relatively rare. The simple selection rules are

$m + n$	Δ	hν
$4q$	*cis–trans* *trans–cis*	*cis–cis* *trans–trans*
$4q + 2$	*cis–cis* *trans–trans*	*cis–trans* *trans–cis*

A most interesting example of what we believe to be a photochemical *cis–trans* cycloaddition is the transformation of a hexatriene into a bicyclohexene. The nodal structure of the lowest π^* level implies a preferred *cis* addition to the diene component, *trans* to the olefin. This conclusion has also been independently reached by W. G. Dauben. For a labeled hexatriene this predicts uniquely one of the four possible isomers.

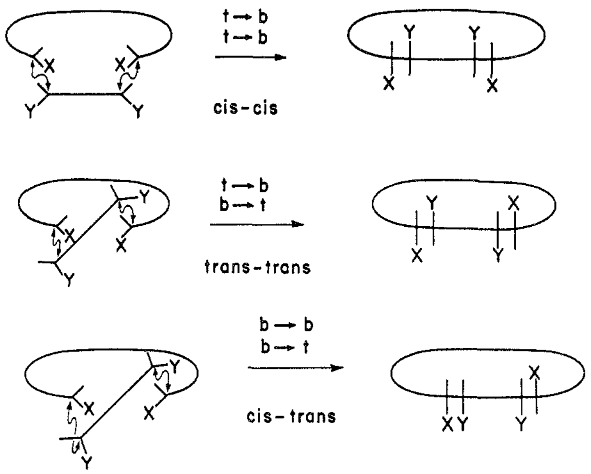
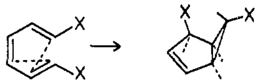
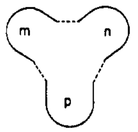


Figure 1. The stereochemical consequences of cycloaddition. The letters t and b indicate top or bottom of the polyene components. Thus the symbol t → b implies that on one side of the cycloaddition one is adding from the top face of the lower component to the bottom face of the upper. The *cis–trans* and *trans–cis* modes are distinct for nonequivalent components but only one of them is shown in the figure.



We believe that further cases of *cis–trans* and *trans–trans* cycloadditions will emerge.

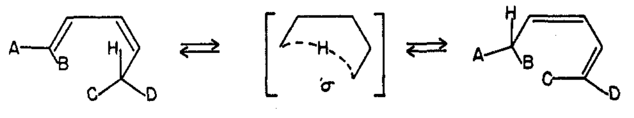
Selection rules for more complicated cycloadditions are easily derived. Thus the triple addition shown below is thermally allowed for $m + n + p = 4q + 2$, photochemically allowed for $m + n + p = 4q$ if the cycloaddition is *cis* on all three components or *cis* on one, *trans* on two. The rules are reversed for a cycloaddition *cis* on two components, *trans* on one, or for one *trans* on all three. The full intricacy of this system would require a very extended discussion—for instance, there are three distinct *cis–trans–trans* cycloadditions even when $m = n = p$.



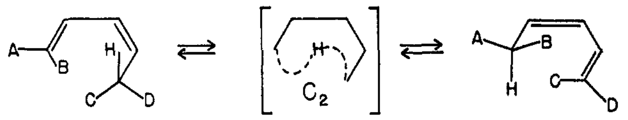
1,3-Dipolar Additions. All of the molecules in this most useful classification scheme are isoelectronic with ozone or nitrous oxide. These molecules have a clearly defined four π-electron system and are thus analogous to allyl anion. An immediate consequence of this electronic structure is that they should add 1,2 to olefins and reclose to a stable three-membered ring in a conrotatory sense. A challenging task is to construct 1,3 or 1,4 dipoles with two or six π-electron systems which should behave in predictably different senses in addition and cyclization reactions. The open-chain dipolar isomer of cyclopropanone is essentially one such species.

Sigmatropic Reactions. We defined as a sigmatropic change of order $[i,j]$ the migration of a σ bond, flanked by one or more π-electron systems, to a new position whose termini are $i - 1$ and $j - 1$ atoms removed from the original bonded loci, in an uncatalyzed 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 sigmatropic migration. These are illustrated below for a [1,5] shift of hydrogen. In the first process, here designated *suprafacial*, the transferred hydrogen atom is associated at all times with the same face of the π system, and the transition state possesses a plane of symmetry. In the second, *antarafacial* process, the migrating atom is passed from the top face of one carbon terminus to the bottom face of the other, through a transition state characterized by a twofold axis of symmetry, C_2. When the migrating group consists of more than one atom the possibility of a topological distinction on it is present as well. The selection rules for a sigmatropic reaction of order $[i,j]$ are



suprafacial



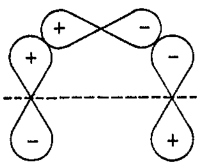
antarafacial

$i + j$	Δ	$h\nu$
$4q$	*antara–supra* *supra–antara*	*supra–supra* *antara–antara*
$4q + 2$	*supra–supra* *antara–antara*	*antara–supra* *supra–antara*

Some specific cases of general interest are shown below.

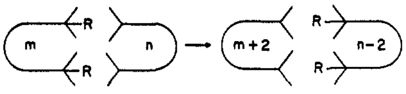
$[i,j]$	Δ	$h\nu$
[1,3]	*antara*	*supra*
[1,5]	*supra*	*antara*
[1,7]	*antara*	*supra*
[3,3]	*supra–supra*	*supra–antara*
[3,5]	*supra–antara*	*supra–supra*

In the derivation of the above rules it has been assumed that a σ orbital of the migrating group interacts with a π system in the transition state and that the migration occurs *with retention of configuration at the shifting site.* If the migrating group possesses an available π orbital and is not so substituted as to create an impossible steric situation in the transition state, then alternative processes can be envisaged using that π orbital and thus proceeding *with inversion* at the migrating center. The selection rules are precisely reversed for such a case.

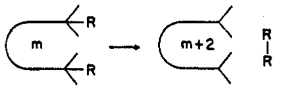


Orbital symmetry arguments are applicable to sigmatropic changes within ionic species. Thus the suprafacial 1,2 shift within a carbonium ion is symmetry allowed and is very well known. The as yet undetected 1,4 migration within a but-2-en-1-yl cation must proceed by an antarafacial transition state, which may be difficult of access. By contrast, it may be predicted that the 1,6 shift should take place through a readily accessible suprafacial transition state.

Eliminations and Group Transfers. The double group transfer shown below will be thermally allowed for $m + n = 4q + 2$, photochemically for $m + n = 4q$, where m and n are numbers of π electrons, q is an integer 0, 1, 2. . . . The best known example of this process

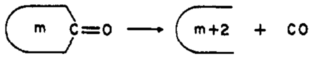


is the diimide hydrogen transfer. The above rule also applies to a process antarafacial on both components and is reversed for a process antarafacial on one component only. The rules may be modified if the possibility of inversion at R is real. The rule also applies to the degenerate case with $n = 0$. We predict that the concerted noncatalytic hydrogenation of a diene, or



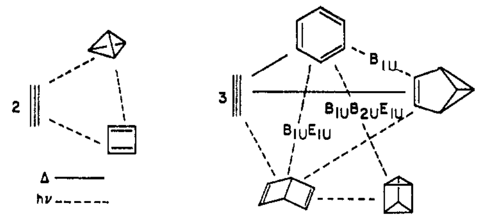
the reverse elimination, should be 1,4 and not 1,2.

The concerted thermal elimination of carbon monoxide or an isoelectronic XY diatomic molecule, or of SO_2, should be thermally disrotatory for $m = 4q + 2$, conrotatory for $m = 4q$, $q \neq 0$.

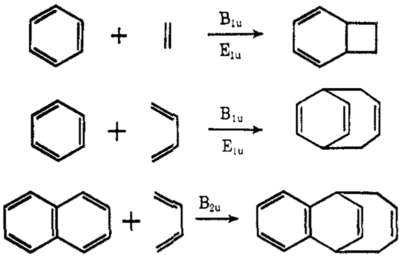


The elimination of the above small molecules in the case in which $q = 0$ is particularly interesting. Our selection rules eliminate the most symmetrical transition state and indicate an unsymmetrical elimination. Some further calculations, however, indicate that some electronic states, in particular the lowest singlet, of a 1,3-diradical can possess significant rotational barriers. The possibility thus arises of a nonconcerted but stereospecific process in this particular case.

The Valence Tautomerisms of $(CH)_n$. We show below the pathways of interconversion of the isomers of cyclobutadiene and benzene. The state labels

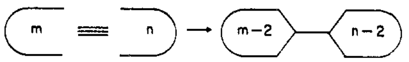


emerging from benzene permit a detailed prediction that different excited states of benzene have different isomerization routes available to them. These conclusions have been independently reached by Longuet-Higgins and Bryce-Smith. The various polyacene excited states should also have different cycloaddition rules.

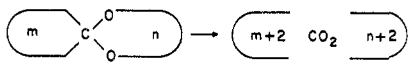


A comment is in order concerning the interpretation of diagrams such as we have drawn above interrelating the benzene isomers. A photochemically allowed pathway does not guarantee that a reaction of the indicated type will in fact be effected. There are many problems in any simple interpretation of photochemical reactions: the excited state may not be the reactive one or excited-state reactions may not be competitive with radiationless decay or with relaxation to an equilibrium excited-state geometry in which all stereochemical information may be lost. Moreover we have little to say without doing further calculations about the relative merits of two or more allowed pathways. However, a photochemically allowed process does carry some assurance of relative thermal stability to interconversion. It is important to keep in mind the word "relative." On an absolute scale Dewar benzene is not very stable with respect to isomerization to benzene, but it is *relatively* extraordinarily stable once one realizes that the enthalpy change for this simple valence tautomerism is about -60 kcal/mole. We wish to claim that in fact Dewar benzene owes whatever stability it possesses to the circumstance that the available isomerizations are symmetry forbidden.

Some Miscellaneous Reactions. The double addition of acetylene to two π systems should be thermal for $m + n = 4q + 2$, photochemical for $m + n = 4q$.



An interesting fragmentation is the elimination of CO_2 from a spiro compound, leaving behind two polyenes. Apparently the only well-characterized example here is the fragmentation of the cyclic ketal of norbornadiene. For the general process one can inquire about the stereochemistry of opening in each polyene,

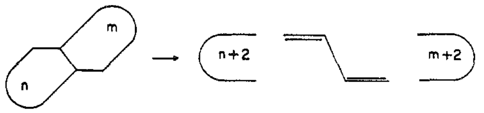


and the amusing conclusion is that, depending on the number of electrons in each component, all possible combinations of stereochemical results may be realized.

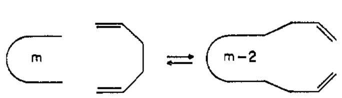
	m	n
$4q + 2$	disrotatory	conrotatory
$4q$	conrotatory	disrotatory

The case with $m = 0$ should not be concerted since a conrotatory creation of an ethylene appears improbable.

It has been implied in the literature that pentalene may decompose to diacetylene and two acetylenes. We find that this should be a thermally forbidden process and that the selection rules for the general fragmentation are the following: the reaction should be disrotatory in both components for $m + n = 4q + 2$. For $m + n = 4q$, $m, n \neq 0$ it may be concerted but either conrotatory or disrotatory. The case $m = n = 0$ should not be concerted, and the case $m = 0, n = 4q, q \neq 0$ may be concerted and conrotatory in the n component.



The reaction shown below with a plane of symmetry bisecting m will be thermally allowed for $m = 4q$, photochemically for $m = 4q + 2$. If a twofold axis is present instead, the rules are reversed.



The oxygen abstraction reaction or its converse should be thermally disrotatory for $m = 4q + 2$, conrotatory for $m = 4q$.