

The Conservation of Orbital Symmetry^[***]

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

1. Introduction

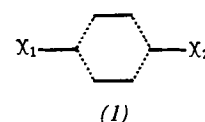
Of the various ways in which the phenomena of chemical bonding have been treated from the theoretical point of view, the molecular orbital method may fairly be deemed to have been the most fruitful in the hands of the organic chemist, and most adaptable to his needs. None the less, the method, with a few conspicuous exceptions, has been used mainly in the study of the static properties of molecules – in ground and excited states – and only rarely have its potentialities been explored in relation to reacting systems.

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 when 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 ap-

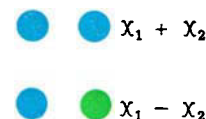
plications made of it, the tests which it has survived, and the corollary predictions which have been verified are already impressive. In this paper we develop our views at some length, survey some of the developments – in our hands and those of others – of the three years just past, and make some new projections.

2. Orbitals and Bonding

It is worth while to review the elementary aspects of the molecular orbital theory of bonding^[5]. Molecular orbitals are constructed as combinations of atomic orbitals, and are then populated by electron pairs. When two equivalent atomic orbitals, χ_1 and χ_2 , combine, they always yield a bonding combination and a corresponding antibonding orbital (1).



The bonding combination is characterized by positive overlap, and by concentration of electron density in the region between the nuclei. By contrast, the antibonding combination exhibits negative overlap, and a nodal surface in the region between the nuclei. When χ_1 and χ_2 are *s* orbitals, the bonding combination is $\chi_1 + \chi_2$, and the antibonding one $\chi_1 - \chi_2$.



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[***] This memoir will also be published as a separate brochure, copies of which can be ordered from Verlag Chemie GmbH, D-694 Weinheim, Postfach 129/149 (Germany), Academic Press Inc., 111 Fifth Avenue, New York, N.Y. 10003 (USA), or Academic Press Inc. Ltd., Berkeley Square House, Berkeley Square, London W. 1 (England), at a price of ca. DM 16.– or \$ 4.40. A German version is also available from Verlag Chemie GmbH.

[1] R. B. Woodward and Roald Hoffmann, *J. Amer. chem. Soc.* **87**, 395 (1965).

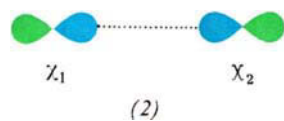
[2] Roald Hoffmann and R. B. Woodward, *J. Amer. chem. Soc.* **87**, 2046 (1965).

[3] R. B. Woodward and Roald Hoffmann, *J. Amer. chem. Soc.* **87**, 2511 (1965).

[4] R. B. Woodward: *Aromaticity*. Special Publication No. 21. The Chemical Society, London 1967, p. 217.

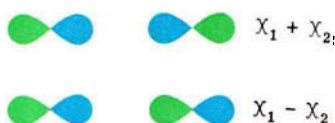
[5] In addition to the classical text by C. A. Coulson (Valence. 2nd ed., Oxford University Press, London 1961), we recommend: C. A. Coulson and E. T. Stewart in S. Patai: *The Chemistry of Alkenes*. Wiley-Interscience, New York 1964, E. Heilbronner and H. Bock: *Das HMO-Modell und seine Anwendung*. Verlag Chemie, Weinheim 1968, and R. S. Mulliken, *Science* **157**, 13 (1967); *Angew. Chem.* **79**, 541 (1967).

When χ_1 and χ_2 are p orbitals interacting in a σ manner, and oriented as shown in (2)

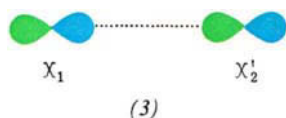


Throughout this paper, the phases of wave-functions are color-coded: positive = blue, negative = green. When phase relationships are not relevant, the orbitals are presented in solid gray.

the bonding combination is again $\chi_1 + \chi_2$ and the antibonding combination $\chi_1 - \chi_2$.



It is important to realize, however, that were the basis orbitals initially arbitrarily oriented in some other



fashion, such as (3), then, since $\chi_2 = -\chi'_2$, 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 minus with minus lobes is precisely equivalent to plus with plus lobes, and $-\chi_1 - \chi_2$ is the *same* bonding orbital as $\chi_1 + \chi_2$.

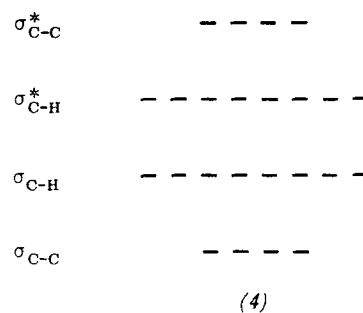


The description of σ bonds in hydrocarbons is simple. Each formal chemical bond engenders a σ and a σ^* orbital. The C–H and C–C cases are:



The molecular orbitals are represented in our drawings as the overlap of two hybrids of unspecified hybridization. It should be emphasized that this is only intended as an artistic mnemonic device: the only essential features of a σ 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.

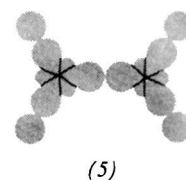
Our simple picture of bonding in, say, cyclobutane, shows four C–C σ levels, and eight C–H σ levels, each with a matching σ^* level (4). The carbon $1s$ orbitals are not considered. Each of the σ levels is occupied by



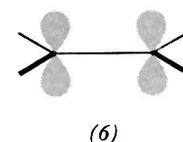
two electrons. Spectroscopic studies indicate that the gap between occupied and unoccupied levels must be of the order of 10 electron volts.

The orbitals we have constructed are semi-localized. They are delocalized over only two atoms. Such orbitals are satisfactory for an analysis of some properties of the molecules – those which depend on all of the occupied molecular orbitals: bond lengths, energies, dipole moments. They are not the proper molecular orbitals of the molecule. The latter are completely delocalized, subject to 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 mechanics of delocalization will be described in Section 3.

In addition to σ bonds, the molecules of organic chemistry contain delocalized π orbitals. Thus, the electronic structure of ethylene is described as follows: There are four σ C–H bonds and a σ C–C bond (5). Each

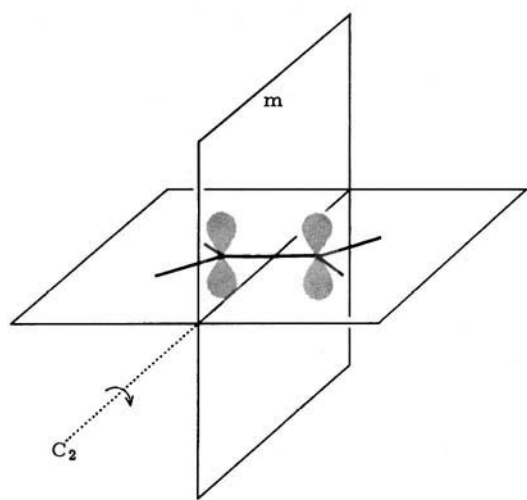


generates a σ and a σ^* level, and five pairs of electrons are placed in the σ levels. There remain two electrons and two atomic p orbitals perpendicular to the plane of the molecule (6). These combine to give π and π^* orbit-



als, differentiated by the absence or presence of a node between the atoms (Figure 1).

There are two independent symmetry operations which may be used to classify these orbitals; the mirror plane m , perpendicular to the molecular plane and bisecting the molecule, and the two-fold rotation axis C_2 , passing through the center of the carbon-carbon bond. It should be noted carefully that the symmetry properties



m C₂

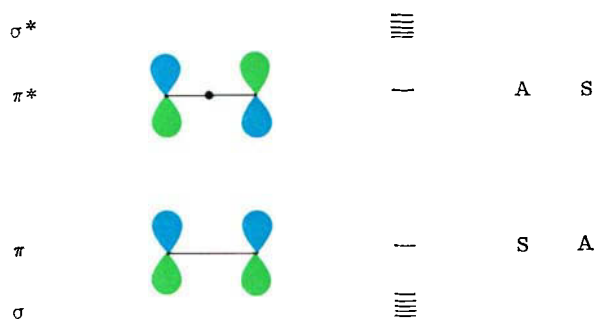


Figure 1. Molecular orbitals of ethylene and symmetry properties of the π and π^* orbitals. A = antisymmetric, S = symmetric. The horizontal bars indicate the relative orbital energies.

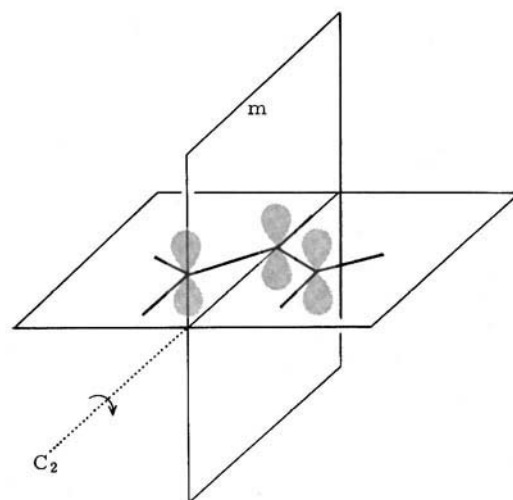
of the ethylene orbitals under each of the above operations are precisely opposite. Thus, the π orbital is symmetric (S) with respect to the mirror plane m , and antisymmetric (A) with respect to the rotation axis C_2 .

The overlap between the two $2p_z$ orbitals is significantly less than that involved in σ interactions, and so the π bond is weaker than a σ bond, and the π and π^* levels are raised and lowered, respectively, from the sea of σ and σ^* levels (Figure 1).

The π molecular orbitals of the three-orbital allyl system are shown in Figure 2. Their nodal structure should be carefully noted. By virtue of their character as π orbitals, they all are 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 at 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 *s-cis* arrange-

[6] Throughout this paper molecular orbitals are symbolized in terms of the atomic orbitals whose interaction gives the actual molecular orbital; since we are in general interested only in nodal properties, we ignore the fact that the coefficients — and thus the relative sizes — of the resultant atomic orbital contributions are not all identical.



m C₂

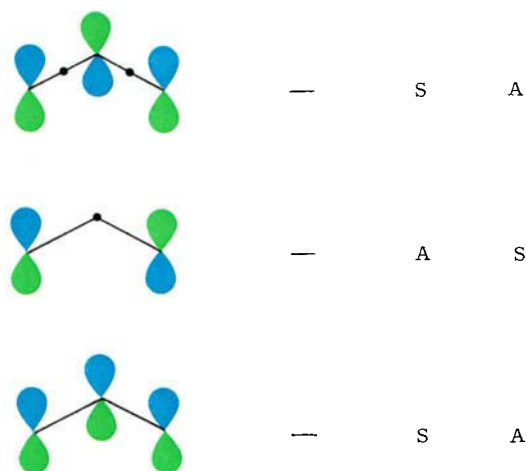
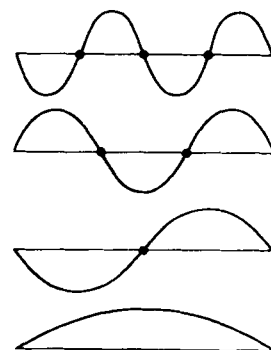


Figure 2. π molecular orbitals of the allyl system. A = antisymmetric, S = symmetric.

ment [6,7]. Note once again the nodal structure and the alternating symmetry properties. The correlation of higher energy with an increasing number of nodes is



(7)

[7] The electronic structure of polyenes is perhaps the most highly developed branch of semi-empirical molecular orbital theory. A very good survey of the field is given in *L. Salem: The Molecular Orbital Theory of Conjugated Systems*. Benjamin, New York 1966. See also *A. Streitwieser: Molecular Orbital Theory for Organic Chemists*. Wiley, New York 1961.

$$C_{ki} = \sqrt{\frac{2}{n+1}} \sin \frac{\pi ki}{n+1}$$

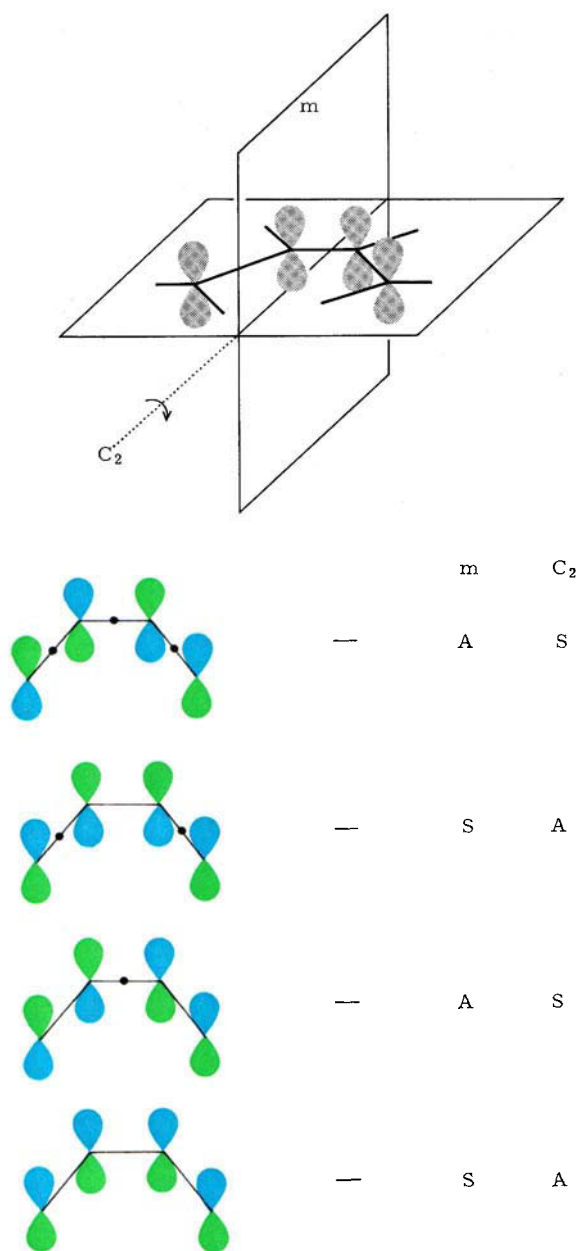


Figure 3. π molecular orbitals of *s-cis*-butadiene. A = antisymmetric, S = symmetric.

not an accident, but rather a general consequence of either classical or quantum mechanics. The envelopes of polyene orbitals coincide with the curve of the wave function of a particle in a one-dimensional box (7). The lowest orbital has no nodes, the next higher one has one node, the next two, and so on until the highest orbital has the maximum number of nodes possible. The general expression for the k^{th} molecular orbital of a polyene or polyenyl system with n carbon atoms is

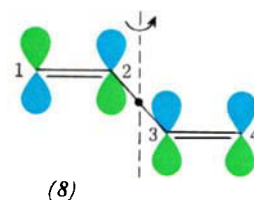
$$\Psi_k = \sum_{i=1}^n C_{ki} \Phi_i$$

where the Φ_i are the atomic orbitals numbered consecutively from one end. The coefficients are given by the expression [7]

The orbitals alternate in symmetry with increasing energy.

If n is even, there are $n/2$ bonding π 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 (8) is symmetric un-



der 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 atoms diatomic correlation diagrams first drawn in the early nineteen-thirties by *Hund* and *Mulliken* have an important place in theoretical chemistry [8]. 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 realistic 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. One then 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, paying due attention to the quantum mechanical non-crossing 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 united atom valuable information was obtained about the level structure of the intermediate region corresponding to the molecule. It was this kind of diagram which provided a

[8] *F. Hund*, *Z. Phys.* 40, 742 (1927); 42, 93 (1927); 51, 759 (1928); *R. S. Mulliken*, *Phys. Rev.* 32, 186 (1928); *Rev. Mod. Phys.* 4, 1 (1932). See also *G. Herzberg*: *The Electronic Structure of Diatomic Molecules*. 2nd edition, Van Nostrand, Princeton 1950.

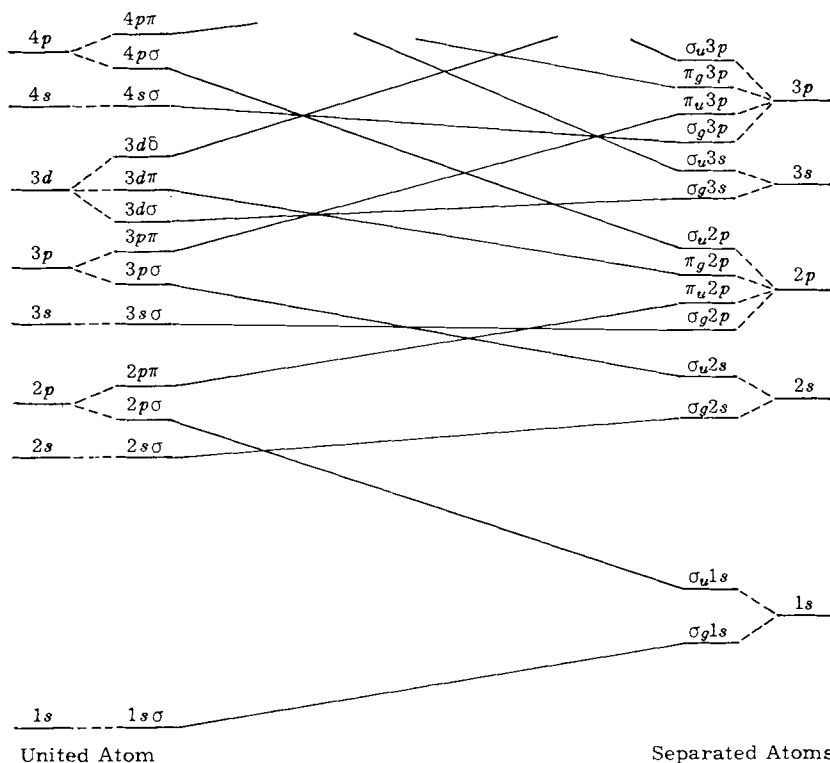


Figure 4. A typical atomic correlation diagram.

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 cycloaddition. On 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 cyclobutane (Figure 5). As usual in theoretical discussions, maximum insight into the problem at hand is gained by simplifying the case as much as possible, while maintain-

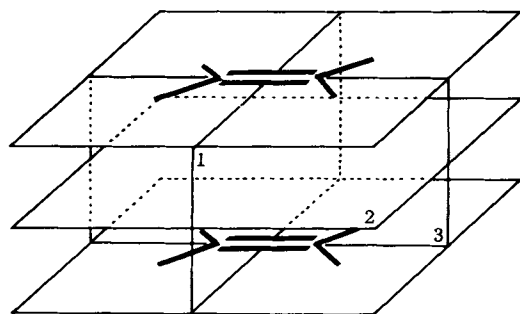


Figure 5. Parallel approach of two ethylene molecules.

ing the essential physical features. In this instance we treat in the correlation diagram *only four* orbitals – the four π orbitals of the two ethylenes. In the course of the reaction these four π orbitals are transformed into four σ orbitals of cyclobutane. We may safely omit the C–H and the C–C σ 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

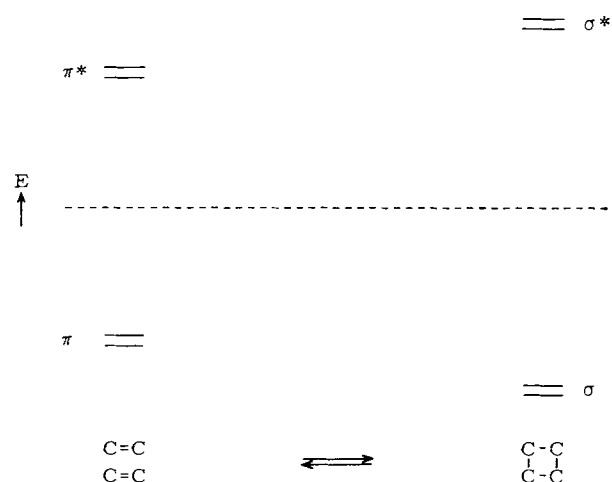
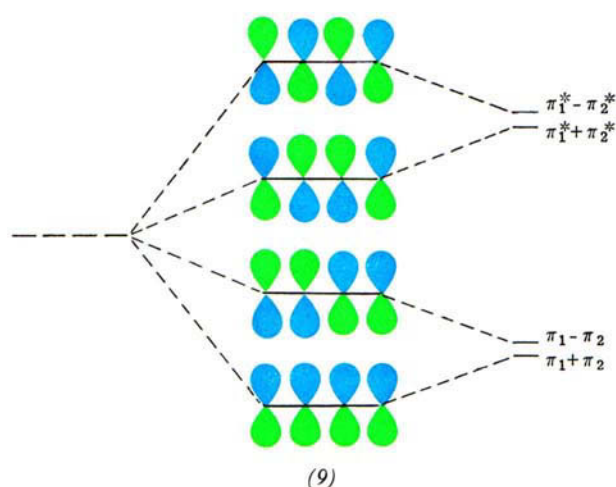


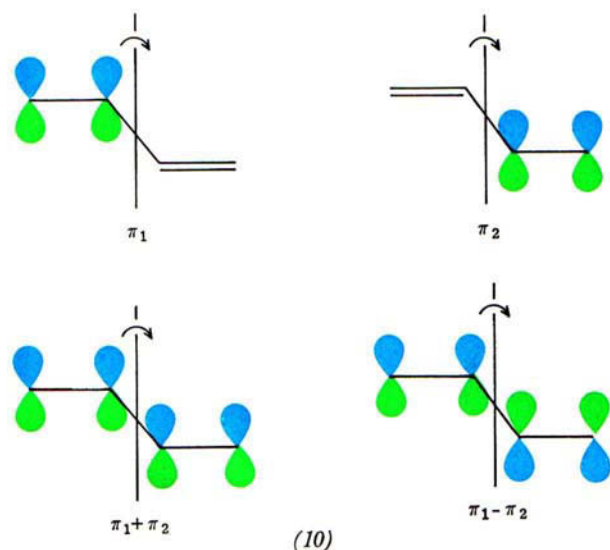
Figure 6. Energy levels of the orbitals essential for the formation of cyclobutane from two ethylene molecules in the geometry shown in Figure 5.

nonbonding level – approximately the energy of an electron in a free carbon $2p$ orbital. We have separated σ and σ^* by an energy greater than that between π and π^* ; 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 π and π^* as approximately 5 electron volts [7].

In the next step the proper molecular orbitals for the reactants and products are written down. A digression on constructing molecular orbitals for interacting systems is in order at this point. Consider an *s-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).

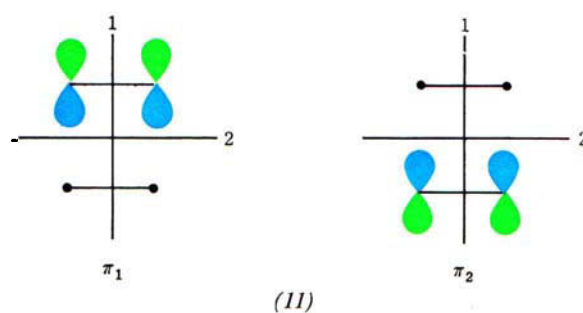


Yet another way is to view butadiene as arising from the interaction of two semi-localized double bonds. Consider the bonding π orbitals of the two ethylenes. While π_1 and π_2 are entirely satisfactory for a description of the isolated double bonds, they are not the

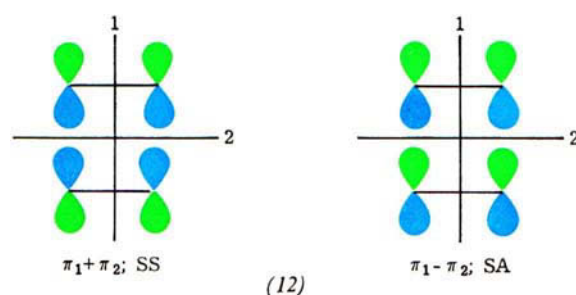


proper combinations to use as molecular orbitals for butadiene. Molecular orbitals must be symmetric or antisymmetric with respect to any molecular symmetry element which may be present. In the case at hand the crucial symmetry operation is a 180° rotation around the two-fold axis. The obvious combinations to use, and ones which do satisfy the symmetry conditions, are $\pi_1 \pm \pi_2$ (10). 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 (cf. Figure 5), diagram (11) represents localized π bonds of the two ethylenes. These are not the proper



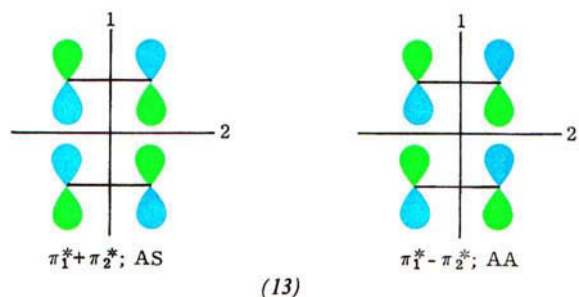
combinations to choose for a discussion of the orbitals of the complex of two ethylenes; they are not symmetric or antisymmetric under reflection in plane 2. Again the obvious combinations are $\pi_1 + \pi_2$ and $\pi_1 - \pi_2$ (12).



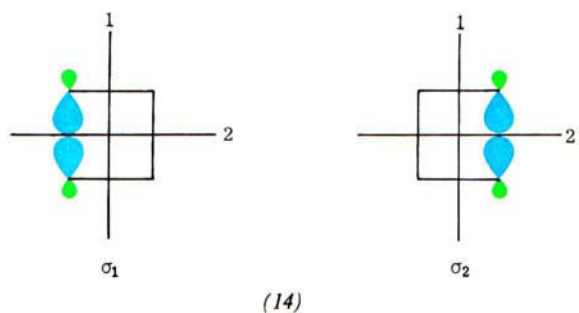
The first of these is symmetric with respect to reflection in both planes 1 and 2 (abbreviated as S_1S_2 or simply SS); the second is symmetric under reflection in plane 1, and antisymmetric under reflection in plane 2 (S_1A_2 or SA) [9]. Both orbitals, of course, are symmetric with respect to reflection in plane 3, and this trivial information need not be explicitly specified. At large separation between the ethylenes, $\pi_1 + \pi_2$ and $\pi_1 - \pi_2$ will be

[9] We could, of course, label the levels with their proper symmetry designations, appropriate to the D_{2h} symmetry of the approach. We deliberately use the symmetric (S) and antisymmetric (A) labels since the nodal properties of the orbitals are then most clearly discernible.

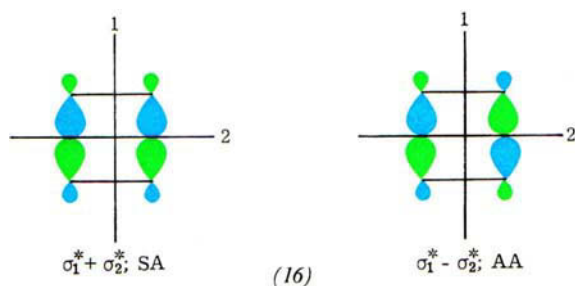
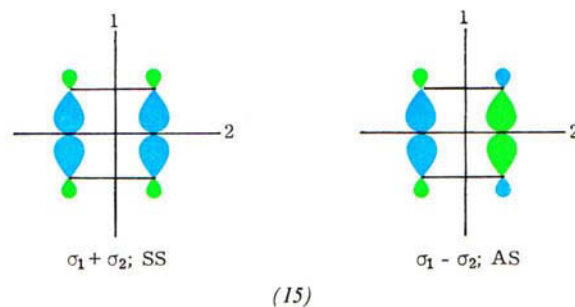
degenerate, but at small separations $\pi_1 + \pi_2$ will be at lower energy than $\pi_1 - \pi_2$ since the former has fewer nodes. Similar combinations of antibonding molecular orbitals for the complex are shown in (13).



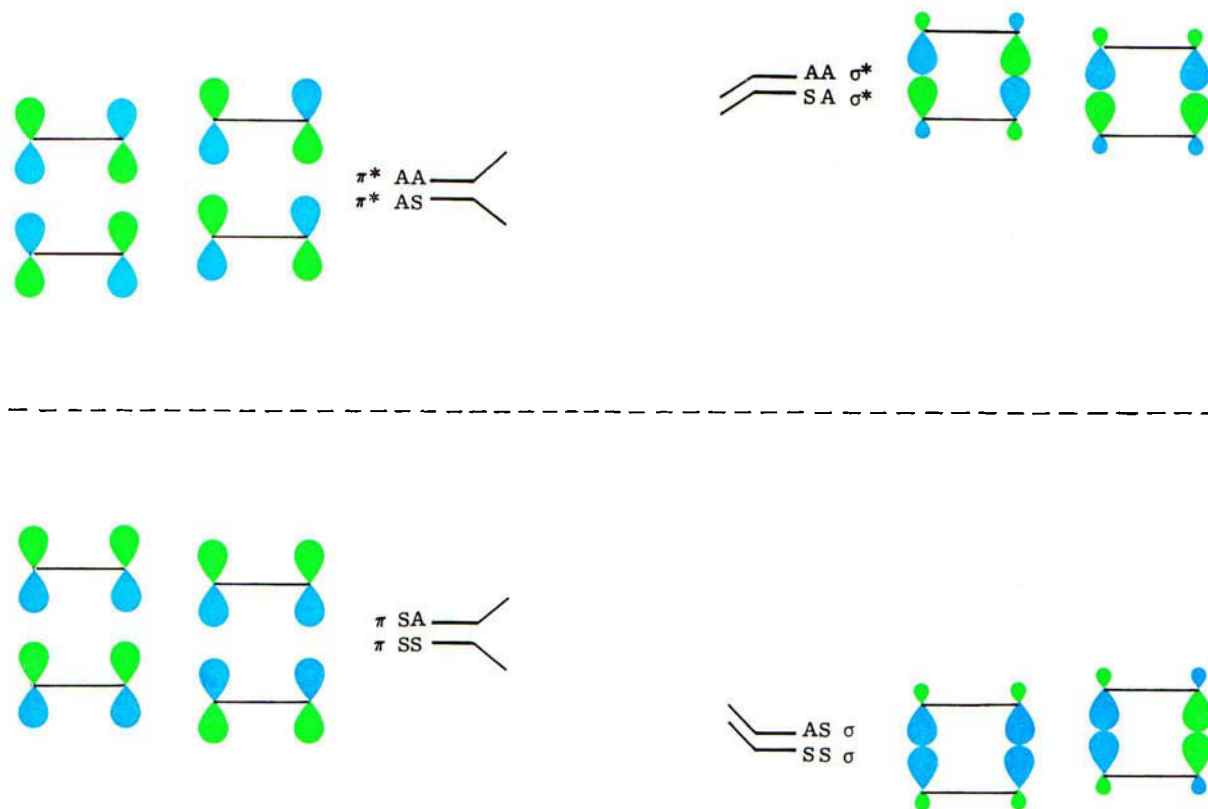
One must next analyze the situation in cyclobutane in an entirely analogous way. Consider the localized σ bonds (14). Again these do not satisfy all the symmetry operations of the cyclobutane molecule, and one must



take the two combinations $\sigma_1 \pm \sigma_2$ (15); a similar procedure must be followed for the antibonding σ^* 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 calcula-



tion, by examining in each case whether any level is bonding or antibonding along the reaction coordinate; in doing this one should keep in mind the definition of bonding or antibonding. Consider the two molecular orbitals for the hydrogen molecule, formed from two $1s$ orbitals (Figure 8). σ_g is bonding because electrons

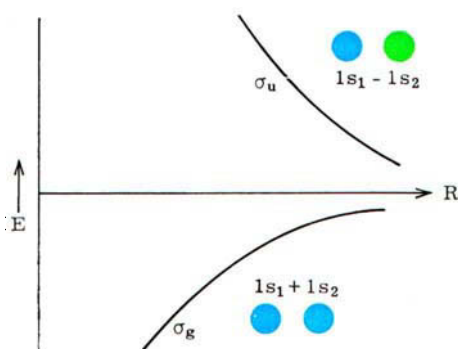


Figure 8. Formation of the bonding (σ_g) and antibonding (σ_u) molecular orbitals of the hydrogen molecule from two atomic $1s$ orbitals.

occupying it lie in the region between and are shared by the nuclei; σ_u is antibonding and at higher energy because the presence of a node between the nuclei isolates electrons populating the orbital in the regions 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_g , $\partial E/\partial R > 0$), while electrons put into an antibonding orbital push

the nuclei apart (that is, for σ_u , $\partial E/\partial R < 0$). 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 inconsequential, but as the distance between the reacting molecules diminishes, this orbital is destabilized and moves to higher energy. Similarly, the antibonding π^* AS orbital becomes bonding in the region of approach. It will thus be stabilized as the reaction proceeds, while the π^* 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 tenet of our treatment of concerted reactions. Clearly, *if orbital symmetry is to be conserved*, two ground-state ethylene molecules cannot

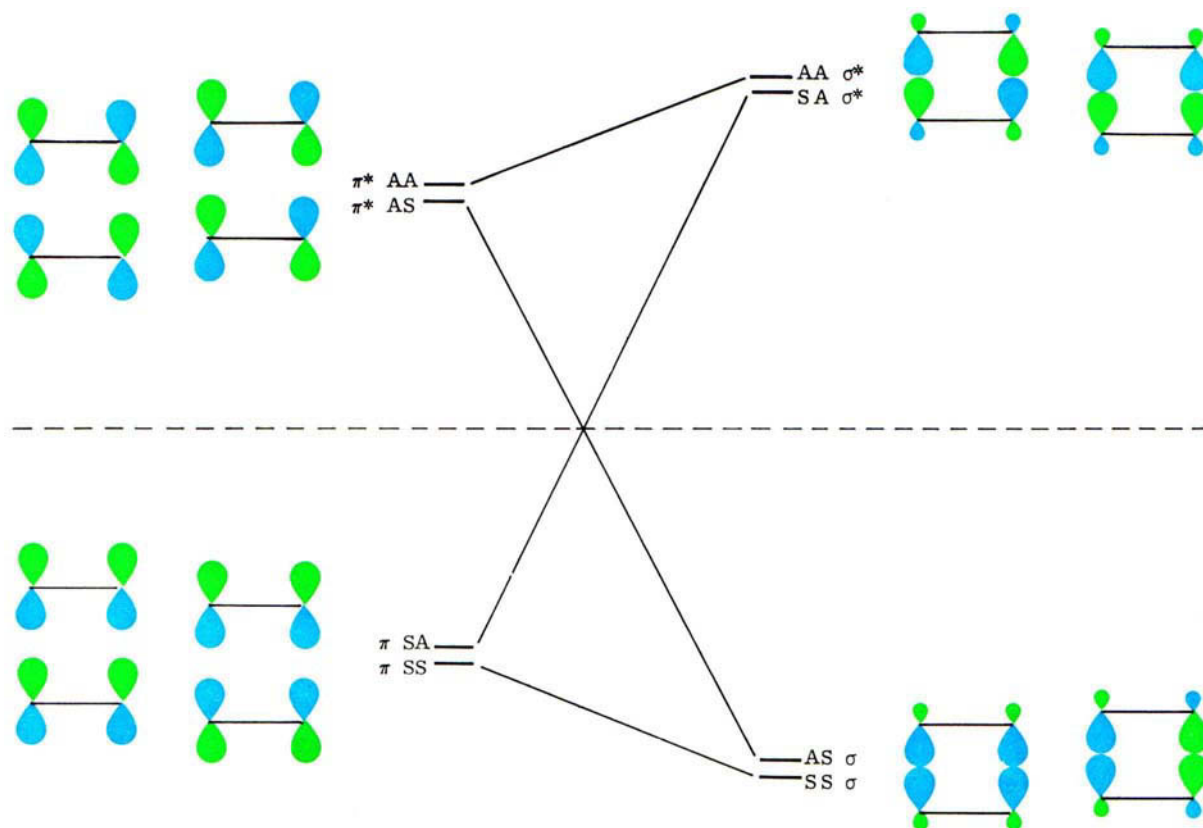


Figure 9. Complete correlation diagram for the formation of cyclobutane from two molecules of ethylene.

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 levels to the non-bonding level – perhaps 5 eV or about 115 kcal/mole.

The lowest excited state of two ethylenes, the configuration $(SS)^2(SA)^1(AS)^1$, 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, singlet-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 so efficient that the chemical changes subsequent to irradiation may be those of a vibrationally excited ground state. Finally,

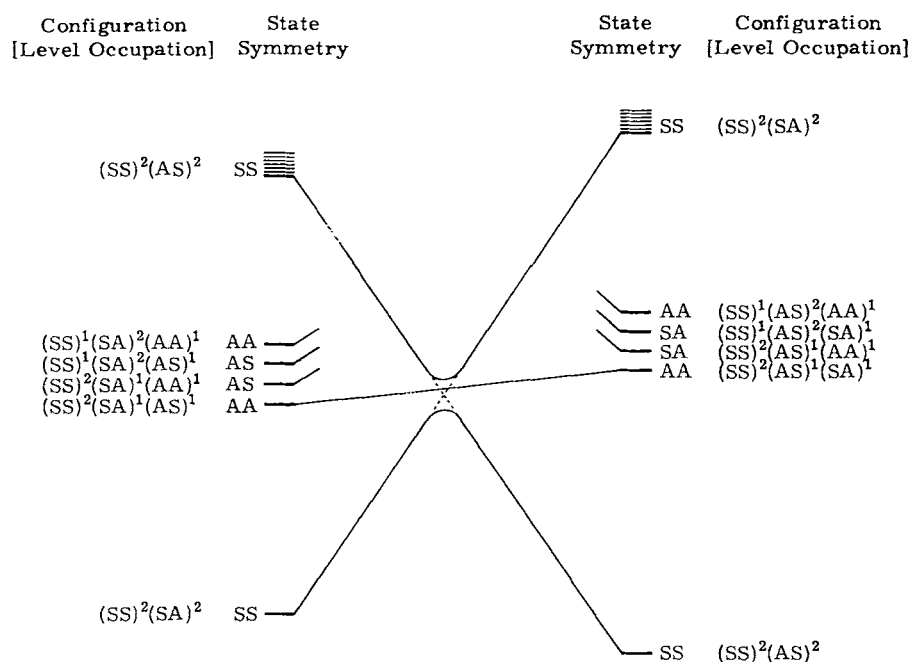


Figure 10. Electronic state diagram for the formation of cyclobutane from two molecules of ethylene. — Note that the symmetry of the states is obtained by multiplying the symmetry labels for each electron, following the rules [7]

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

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

Only singlet excited states are shown, and at this level of sophistication they should be regarded as degenerate in both reactants and products.

will prevent the resulting crossing, and force a correlation of ground state with ground state. But in the actual physical situation, the reaction still must pay the price in activation energy for the intended but avoided crossing. An order of magnitude estimate of the symmetry-imposed energy barrier to the concerted face-to-

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 punctilios in any way vitiates the consequences of orbital symmetry

control. The principle of conservation of orbital symmetry remains applicable, *provided that the chemically reactive excited state is identified*; 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 11).

The essential levels involved in the reaction are now six in number, and they are illustrated in the correlation diagram shown in 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 consequen-

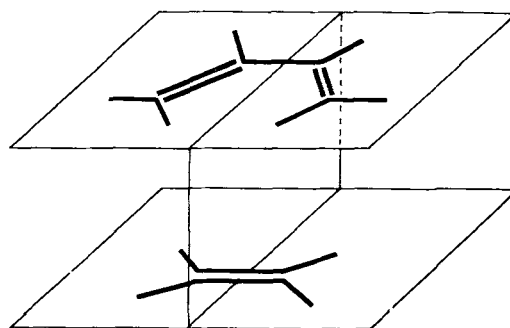


Figure 11. Symmetric approach of butadiene and ethylene in the Diels-Alder reaction.

tial. On the product cyclohexene side note that one must construct delocalized σ bond combinations just as was done for cyclobutane.

The difference between this 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.

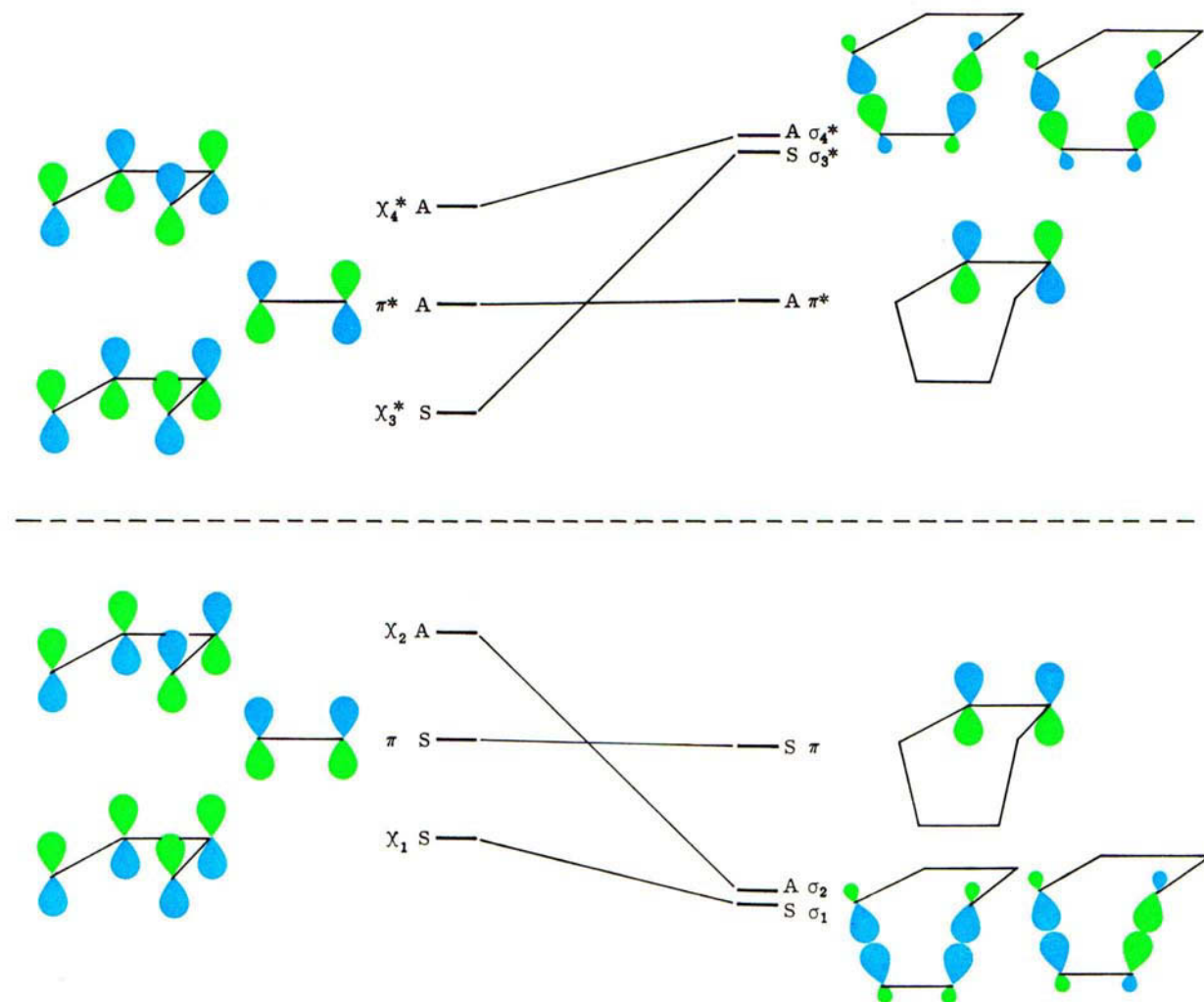


Figure 12. Correlation diagram for the Diels-Alder reaction of butadiene with ethylene.

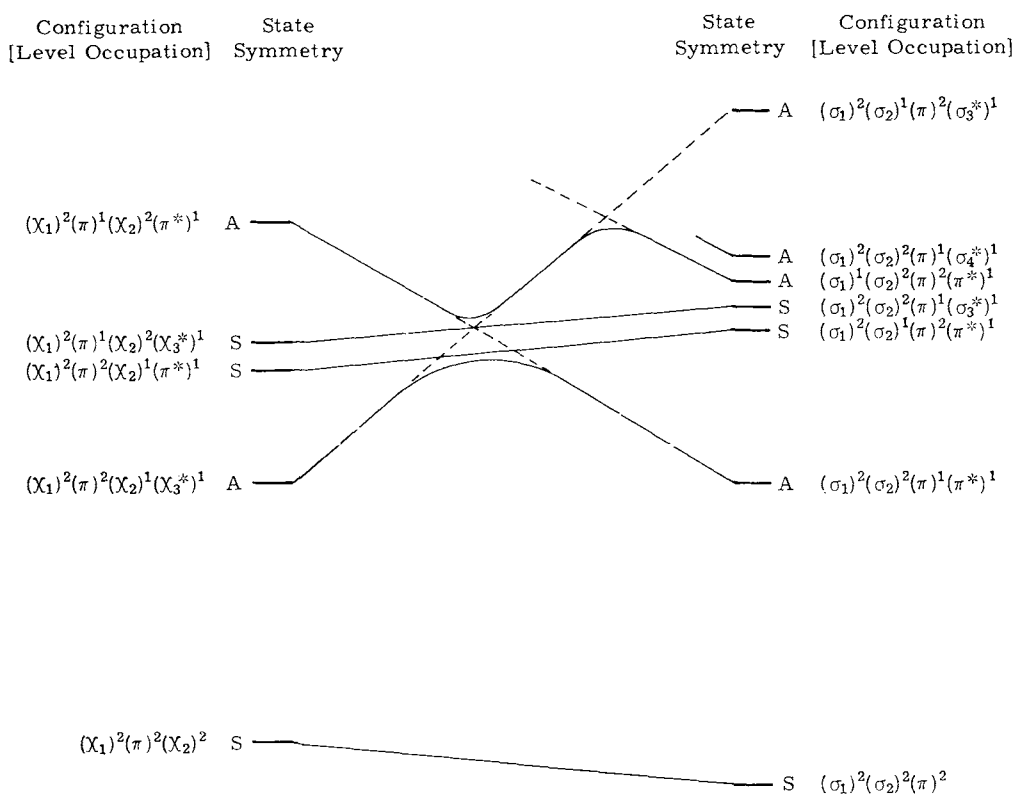


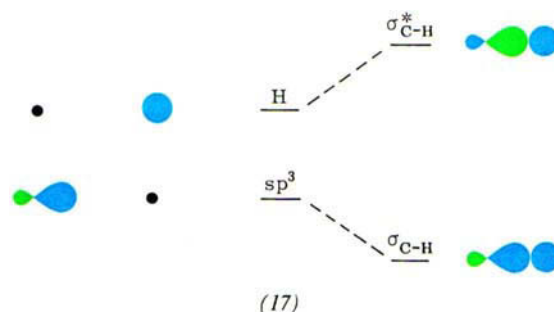
Figure 13. Electronic state diagram for the Diels-Alder reaction of butadiene with ethylene.

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 approximate 20 kcal/mole – which arises from factors not simply related to orbital symmetry conservation; among them are energy changes accompanying rehybridization in the levels we have not included, and bond length extensions and contractions, as well as angle distortions.

The first excited state of the diene-ethylene complex does not correlate with the first excited state, $\pi \rightarrow \pi^*$, of cyclohexene. Consequently, in this case a symmetry-imposed barrier arises in the excited state process. These circumstances are perhaps most simply apprehended when it is realized that the first excited state is formed by promotion of an electron from an orbital decreasing in energy along the reaction coordinate to one increasing in energy.

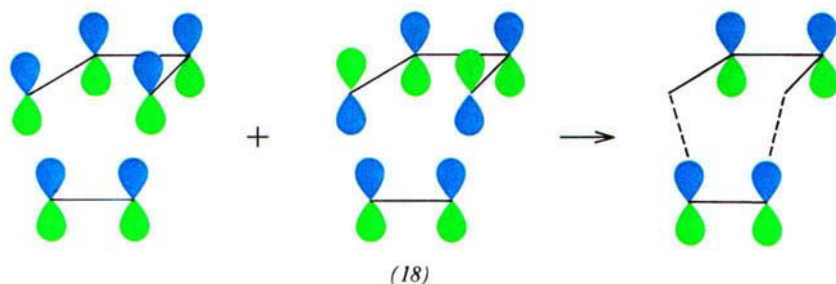
The physical correlations of some levels may seem non-intuitive, but in each case they are realistic, and can be understood if followed through carefully in detail. For instance, it may seem strange that an ethylene π level becomes a π level of the cyclohexene. To understand this relationship one must allow the ethylene π level to interact with the two other symmetric levels – the lowest occupied and lowest unoccupied diene levels. An important general rule of quantum mechanics is rele-

vant here^[10]: 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 more than 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 σ bond from a carbon sp^3 hybrid and a hydrogen $1s$ orbital (17). In the case of butadiene + ethylene we



find that the olefin π level mixes into itself χ_1 in an antibonding way and χ_3 in a bonding way (18). The diene contributions cancel at C-1 and C-4 of the buta-

[10] The rule follows directly from perturbation theory and the correlation of higher energy with increasing number of nodes in a wave function.



diene, 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 moieties.

If one considers further cases of the general cycloaddition reaction of an m π -electron system with an n π -electron system to form two new σ 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-allowed for ground states and symmetry-forbidden for excited states;

b) those similar to that for the ethylene + 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 π orbitals in a reactant, there will be $m/4$ symmetric bonding π orbitals if $m/2$ is even, or $(m+2)/4$ if $m/2$ is odd. That part of the product derived from this component will contain $(m-2)$ π orbitals, of which $m/4$ are symmetric bonding levels if $m/2$ is even, or $(m-2)/4$ if $m/2$ is odd. There are three possible cases (q_1 and q_2 are integers = 0, 1, 2...):

Case	m	n	Total Symmetric Bonding π Levels	
			Before	After
1	$4q_1$	$4q_2$	q_1+q_2	q_1+q_2
2	$4q_1+2$	$4q_2$	q_1+q_2+1	q_1+q_2
3	$4q_1+2$	$4q_2+2$	q_1+q_2+2	q_1+q_2

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

$$m+n=4q_1+4q_2+2=4q+2.$$

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

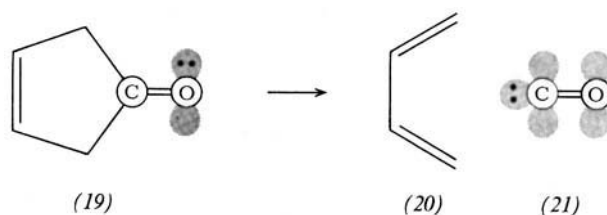
$$m+n=4q_1+4q_2 \text{ or } 4q_1+4q_2+4=4q$$

are symmetry-forbidden. In each case, of course, these rules are precisely reversed for reactions involving excited states. Further, it must be emphasized that these deductions apply only to cases in which the geometry of approach 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

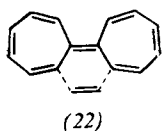
A crucial phase in the construction of a correlation diagram is the identification of pertinent σ and π levels and their delocalization to the full extent required by the transition state symmetry. The simplest procedure may be formulated as follows:

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

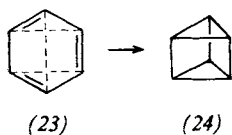


are bonding, a new CO bond and its π^* counterpart, and a new nonbonding pair level on the carbon atom of the carbon monoxide. Left out of consideration as non-essential are another oxygen lone pair and the remaining C=O π bond. Note that there exists an auto-

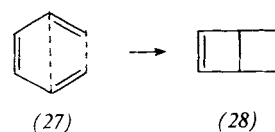
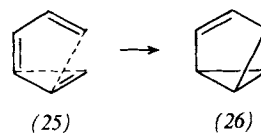
matic check in that the number of levels of each symmetry type on the right-hand side of a correlation diagram must equal that on the left.



b) If a polyene system is present, the proper molecular orbitals of a polyene should be used. Thus, in the cycloaddition of a heptafulvalene (22), one should consider the orbitals of a fourteen-membered polyene.

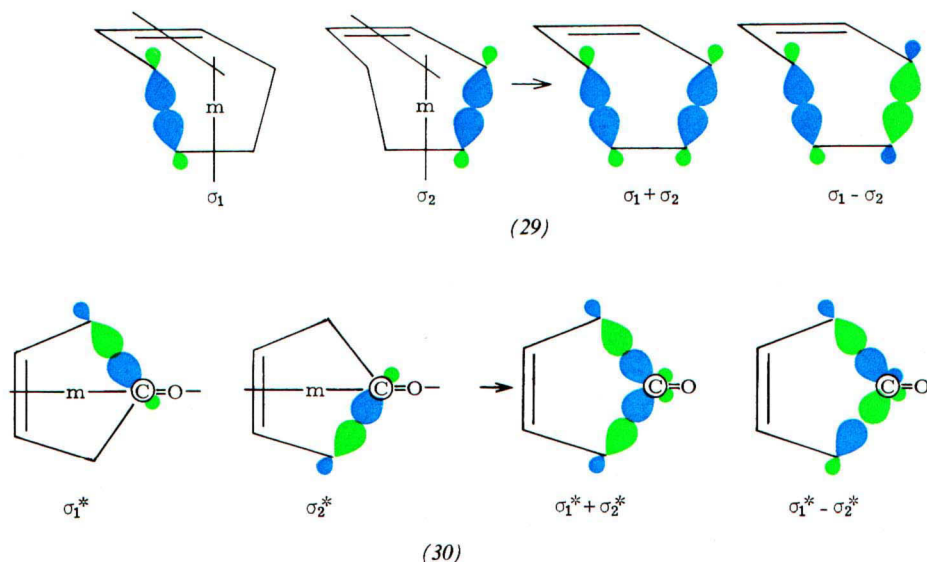


For the cyclization of benzene (23) to prismane (24), the proper orbitals on the left are those of benzene [cf. Section 6.4].



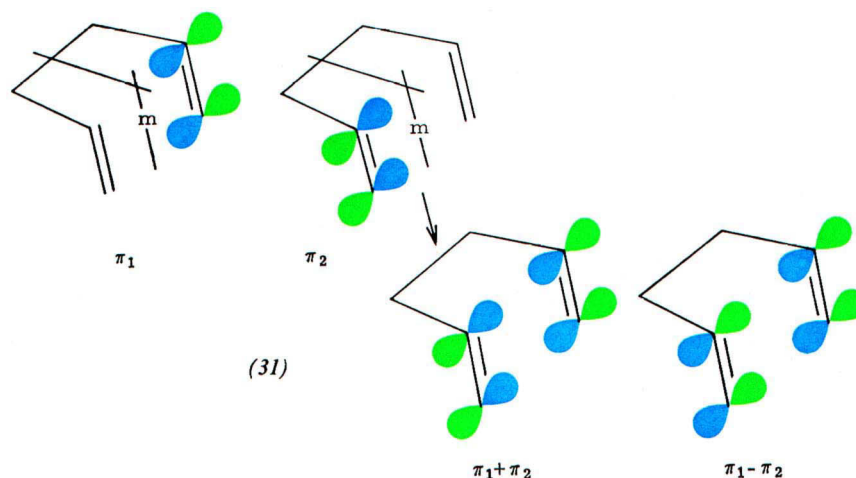
bicyclo[2.2.0]hexene (28) must be treated as [4+2] and [2+2] cycloadditions respectively.

c) Mix all bonding σ orbitals which are not symmetric or antisymmetric with respect to every molecular symmetry element until they become so. For the vast majority of cases this process is one of identifying the symmetry-related orbitals, and forming their sums and differences. The procedure should then be repeated for σ^* levels. As one example, consider the newly-formed σ bonds of a cyclohexene – the product of a [4+2] cycloaddition. The symmetry-related σ orbitals are



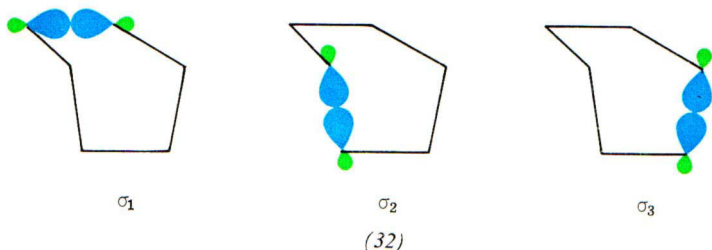
However, if only fragments of a polyene system participate in a reaction, the molecular orbitals of the component fragments must be used. Thus, the conversion of a hexatriene (25) to a bicyclo[3.1.0]hexene (26), or to a

σ_1 and σ_2 ; they must be transformed as indicated in (29), to $\sigma_1 + \sigma_2$ and $\sigma_1 - \sigma_2$. Again, consider the σ^* orbitals of cyclopentenone (30).

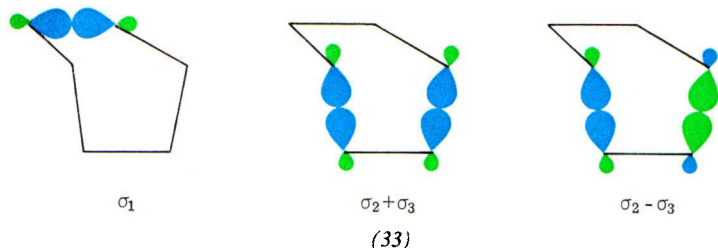


A similar mixing is required for nonconjugated π levels. Thus, in considering a [2+2] cycloaddition within a 1,5-hexadiene, leading to a bicyclohexane, the preparation of π orbitals is performed as shown in (31).

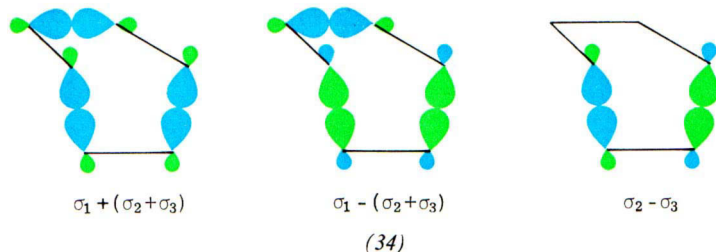
d) A convenient, but not necessary, further step is to mix with each other all orbitals of a given symmetry. For example, consider the σ bonds of a [2+2+2] cycloreversion of a cyclohexane to three ethylenes. Assume a boat conformation of the cyclohexane. The three localized σ orbitals are σ_1 , σ_2 , and σ_3 (32). The



only symmetry element in the transition state is a plane bisecting σ_1 . The orbital σ_1 is symmetric under reflection in that plane, but σ_2 and σ_3 are not. Thus, in accordance with rule c) above, we should form the delocalized combinations $\sigma_2 + \sigma_3$ and $\sigma_2 - \sigma_3$. This yields a new set of symmetry-adapted orbitals (33).



Now σ_1 and $\sigma_2 + \sigma_3$ are symmetric with respect to the symmetry plane, and it is convenient to delocalize further by taking their sum and difference (34).



More extensive delocalization (a secondary effect – but one which can be of chemical significance) would follow from mixing of σ_1^* and $\sigma_2^* - \sigma_3^*$ into $\sigma_2 - \sigma_3$, and $\sigma_2^* + \sigma_3^*$ 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 one 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 corollaries:

(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 [cf. 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 inherent symmetry. Thus, if there are heteroatoms in a polyene component, they are to be replaced by their isoelectronic carbon groupings. 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 cubane from cyclooctatetraene in one step (Figure 14).

Construction of a correlation diagram (Figure 15) without regard to precaution a) would lead to the con-

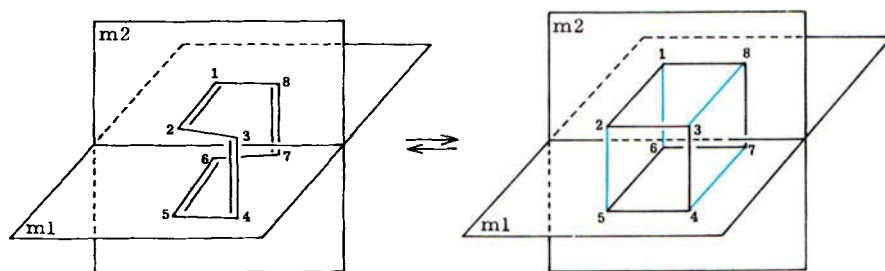


Figure 14. Formation of cubane from cyclooctatetraene in a concerted reaction.

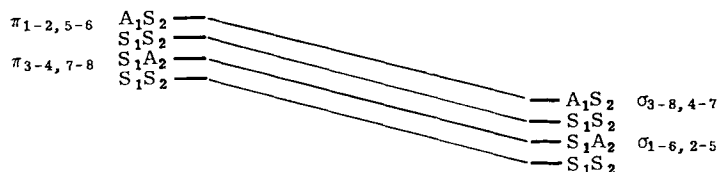
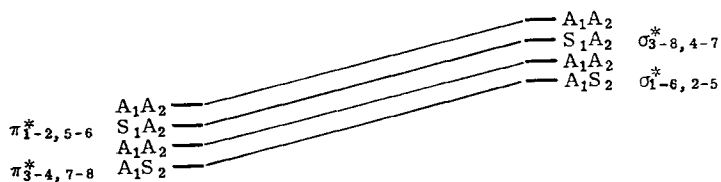


Figure 15. Incorrect correlation diagram for the formation of cubane from cyclo-octatetraene.

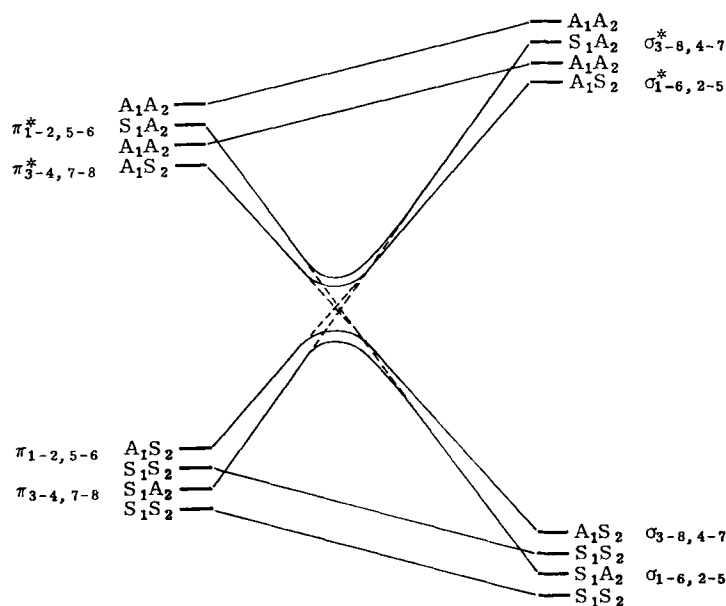


Figure 16. Correct correlation diagram for the formation of cubane from cyclo-octatetraene. — Within any of the four groups of four closely spaced levels, those with both symmetric and antisymmetric labels, regardless of subscripts, are in fact degenerate, though shown here for clarity as differing slightly in energy.

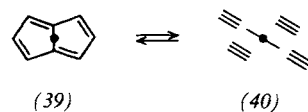
clusion that this superposition of two [2+2] cycloadditions should be a symmetry-allowed thermal process.

In fact the diagram should really appear as in Figure 16. The intended correlation of the S_1A_2 orbital formed from $\pi_{3-4,7-8}$ is to an antibonding $S_1A_2 \sigma_{3-8,4-7}^*$ orbital. 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 S_1A_2 orbital of the cu-

bane. 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 height of the electronic hill that reactant or product orbitals must climb in reaching the transition state; and the presence or absence of a hill is a function of the *intended* correlation, or the initial

slope of the levels. From this point of view, we see that in the case at hand the 3-4,7-8 combination is in no wise facilitated by the concurrent 1-2,5-6 process, and *vice versa*.

An example of type b) is provided by consideration of the conversion of butadiene (35) to bicyclobutane (36). Here the only molecular symmetry element is a



The rationale for point c) will become apparent on comparison of the correlation diagram for the face-to-face addition of ethylene to ethylene with that for ethyl-

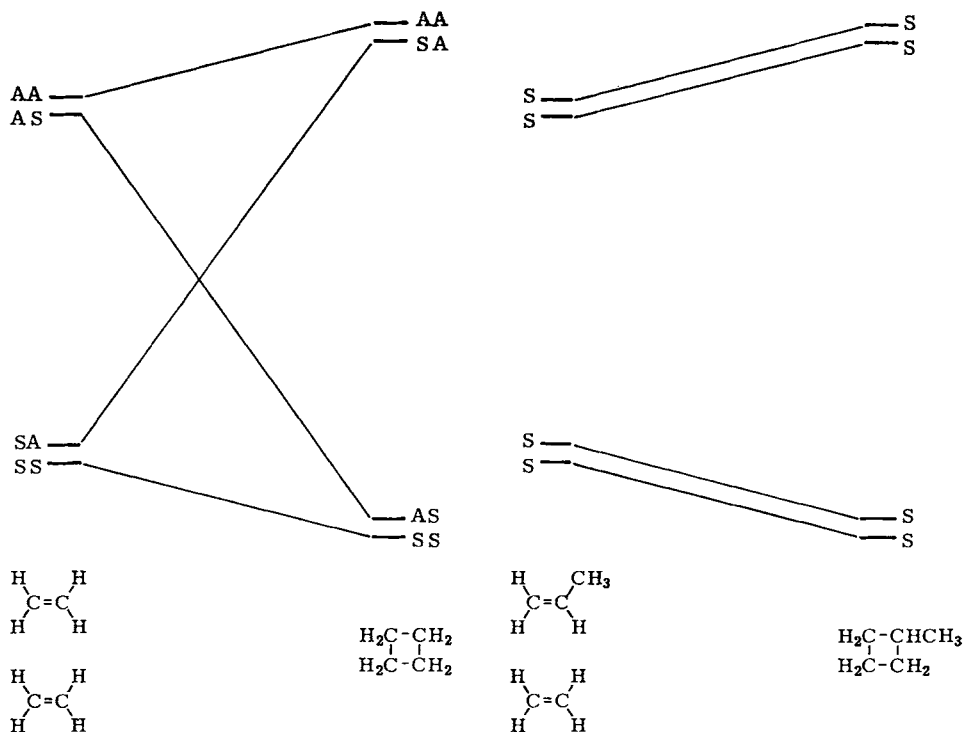
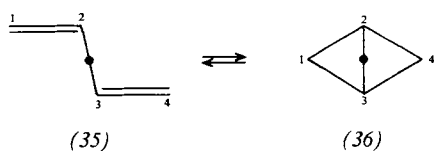
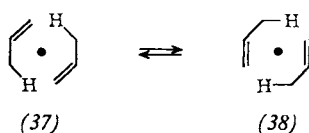


Figure 17. Left: Correlation diagram for the cycloaddition of two ethylene molecules. — Right: Incorrect correlation diagram for the cycloaddition of ethylene to propylene.

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 hydrogens [(37)→(38)], where only a center of symmetry (passing through no bonds) could be present.



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

ene to propylene. For the latter case there is, strictly speaking, no symmetry in the transition state. Thus, all levels are trivially symmetric and one might be tempted to draw the correlation diagram as shown at right in Figure 17.

The conclusion would be that methyl substitution had made the thermal [2+2] cycloaddition symmetry-allowed. This is incorrect. The proper level correlation diagram is shown in Figure 18.

Methyl substitution has in an absolute sense reduced all levels to the same symmetry. The level crossing has become impossible. But the perturbation is a very small one and so the crossing is barely avoided. A bonding level of reactants has still moved to high energy in the transition state. The corresponding state diagram differs trivially from that for ethylene + ethylene. The reaction remains symmetry-forbidden [11].

[11] A similar situation arises in other areas of chemistry. The $n \rightarrow \pi^*$ transition in formaldehyde is electric-dipole forbidden. The source of the small intensity observed is still disputed. In the cases of acetaldehyde, or of unsymmetrically substituted ketones, the symmetry element which made the formaldehyde transition electric-dipole forbidden is removed. The transition becomes allowed. Does it therefore jump to a high intensity? Not at all; the intensity remains practically unchanged. This is because the *essential* symmetry, that of the local environment of the carbonyl group, is unchanged.

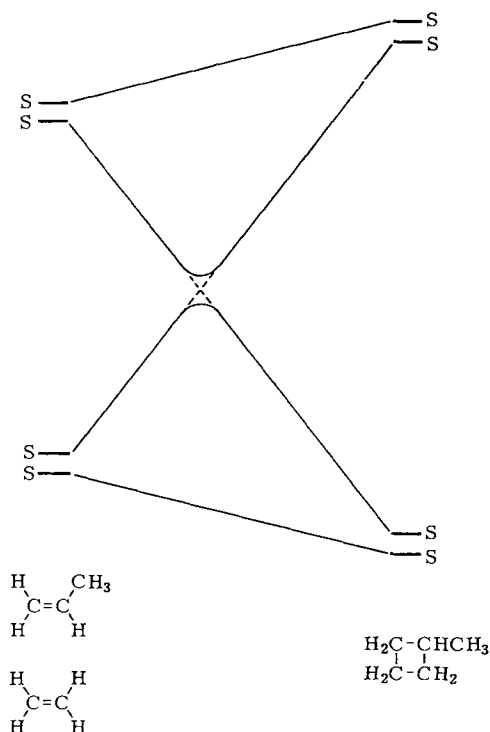


Figure 18. Correct correlation diagram for the cycloaddition of ethylene to propylene.

4. The Conservation of Orbital Symmetry

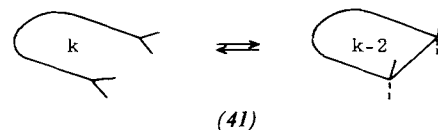
It is clear that the absence or presence of molecular symmetry in an absolute sense cannot be the ultimate source of the allowedness or forbiddenness of a reaction. Symmetry is discontinuous. It is either on or off, here or not here. Chemistry is obviously not like that. A slight perturbation, say substitution 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 crutch to aid us in denominating those 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 asymmetry of the components (*e.g.*, in the "ene" 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 *pari passu* from real crossings 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 reactants, it must be related to an antibonding reactant orbital. Whether or not it ac-

tually correlates to that antibonding orbital is dependent on the presence or absence of total symmetry; but even if the intended correlation is foiled, the level soars to high energy in the transition state.

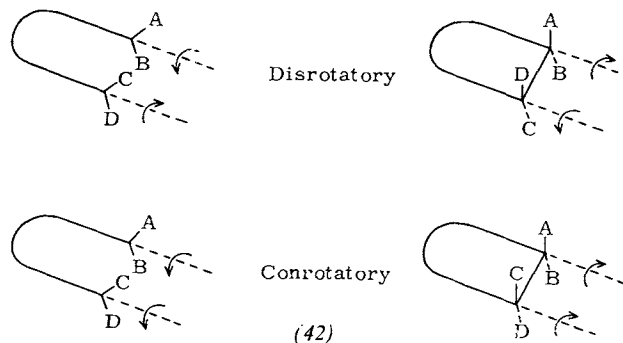
In short, the most general, and at the same time physically most realistic view of orbital symmetry control of chemical reactions is obtained by specifying the relevant molecular orbitals of reactants, and observing their corresponding form in products, as reaction occurs *with conservation of orbital symmetry*. To illustrate our method at work 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

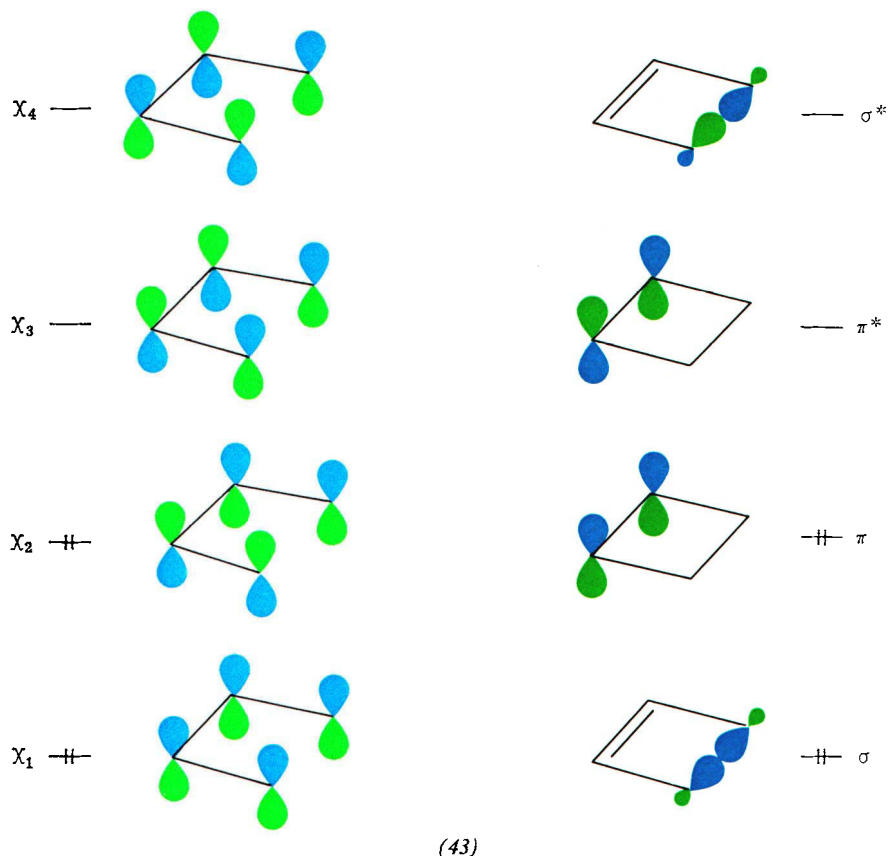
These intramolecular cycloadditions provided the stimulus for our study of molecular orbital symmetry and concerted reactions. We define as *electrocyclic reactions* the formation of a single bond between the termini of a linear system containing k π electrons, and the converse process (41).



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 *disrotatory* 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.

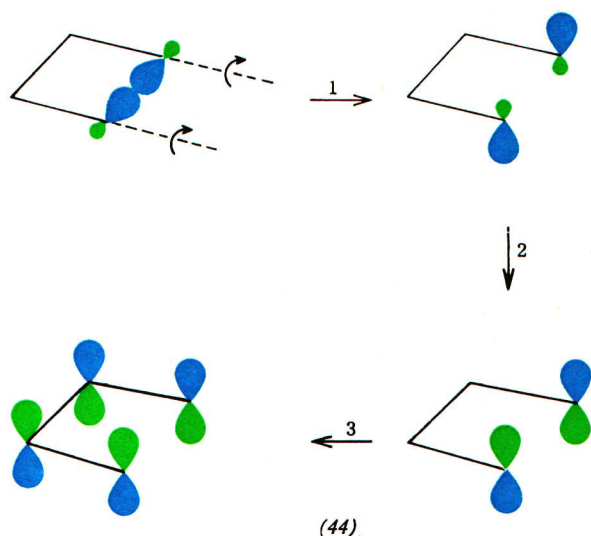


Consider the essential molecular orbitals in the conversion of cyclobutene to butadiene. These are the four π orbitals of the butadiene $\chi_1, \chi_2, \chi_3, \chi_4$, the π and π^* lev-



els of the cyclobutene double bond, and the σ and σ^* orbitals of the single bond to be broken (43).

Consider carrying out a conrotatory motion to completion on σ [step 1 in (44)] and follow through with a rehybridization (step 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 (step 3) of orbitals at C-2 and C-3.



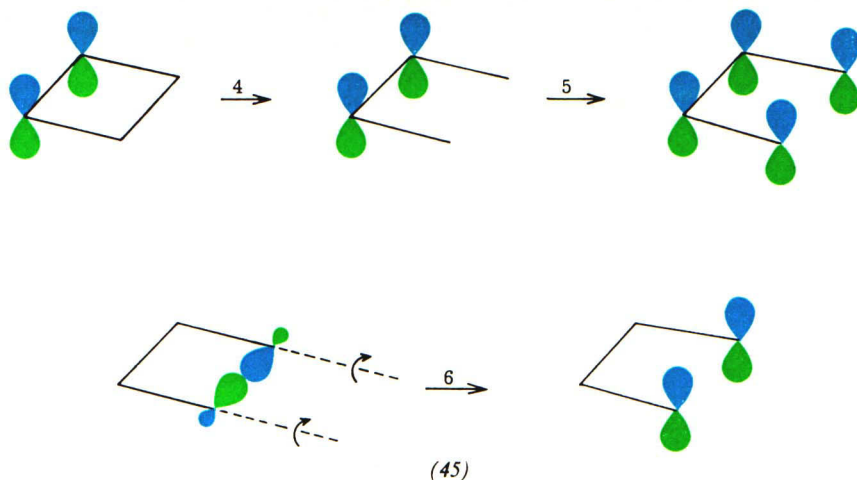
It should be kept in mind that in reality the steps 1, 2, and 3 will all be simultaneously proceeding along the reaction coordinate, and that the above factorization is only an aid to visualization. The growing-in of step 3

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 π^* with σ as the reaction proceeds. We have now followed σ through the reaction and correlated it with another bonding orbital, χ_2 . Similarly we follow π through (45). Note here that the growing-in step 5 is really a mixing of π with σ^* (cf. step 6). π thus correlates with χ_1 .

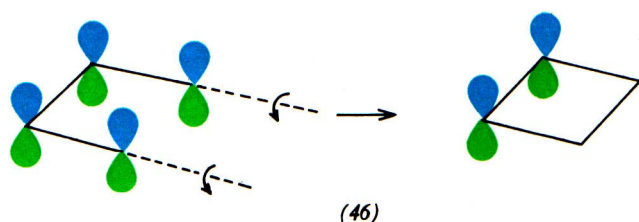
The correlations could of course have been obtained starting from butadiene. χ_1 by a conrotatory motion becomes π (46) and χ_2 is transformed into σ (47).

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 is again a result of mixing with higher orbitals of the proper symmetry. Very similar arguments lead to a correlation of σ^* and χ_3 , and of π^* and $-\chi_4$ ($\equiv \chi_4!$). We have thus achieved a correlation of bonding levels of the reactant with bonding levels of the product, with conservation of orbital symmetry. The thermal reaction should be a facile one.

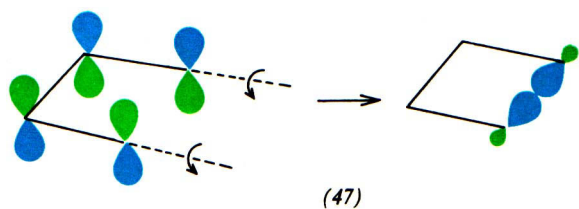
By contrast, consider now a disrotatory opening. The correlations are indicated in (48). Both σ and π must correlate with χ_1 or χ_3 ($\equiv -\chi_3!$). But since only one can correlate with χ_1 , the other must go up to χ_3 , which is antibonding. Conservation of orbital symmetry requires in this case a high-lying transition state and the



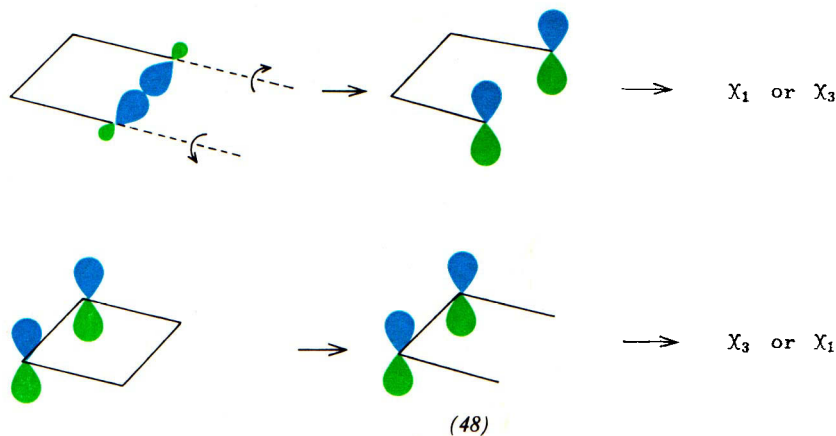
thermal reaction is symmetry-forbidden. Again the problem could have been approached from the other side (49).



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 equivalent to the construction of two level correlation diagrams (Figure 19). It is clear that in the conrotatory process a two-fold rotation axis is main-

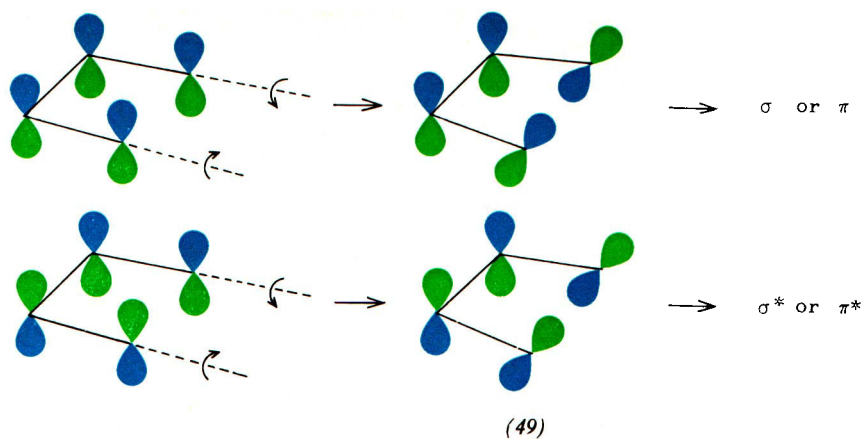


tained at all times whereas in the disrotatory motion an invariant plane of symmetry is present. These diagrams are clearly analogous to those discussed in section 3 (above) for combination reactions of π electron systems. Obviously the diagram for the conrotatory process is characteristic of a symmetry-allowed 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 derivation 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 perturbed during incipient reaction. In this sense their role has been stressed in the important work of Fukui^[12]. Second, if there is little symmetry in a molecule and if there is a bonding level which is intending to cross the energy

[12] K. Fukui, T. Yonezawa, and H. Shingu, *J. chem. Physics* 20, 722 (1952); K. Fukui, T. Yonezawa, C. Nagata, and H. Shingu, *ibid.* 22, 1433 (1954); K. Fukui in O. Sinanoğlu: *Modern Quantum Chemistry*. Academic Press, New York 1965, Vol. 1, p. 49, and references therein.



gap to correlate to an antibonding level, then that level will usually be the highest occupied level. Consequently, its motion determines the course of the cor-

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, repulsive 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, attractive interaction terminating in the actual formation of the new σ bond.

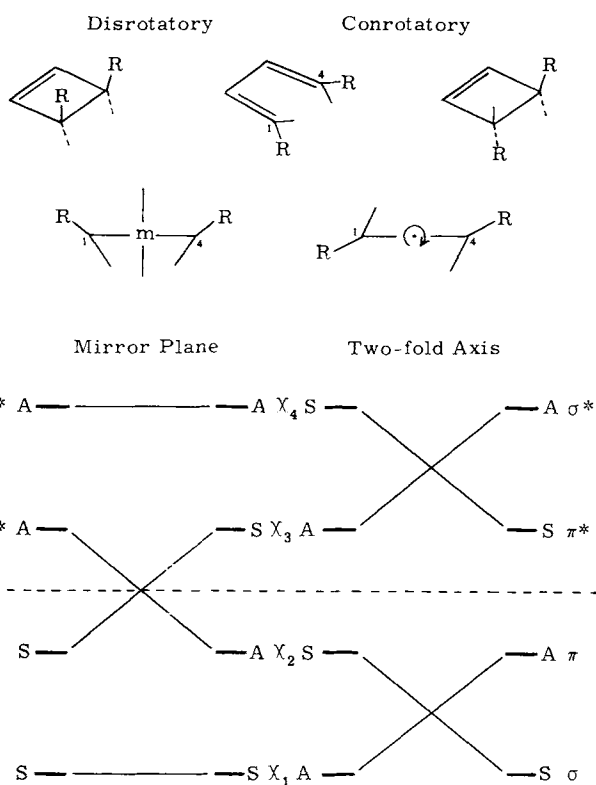


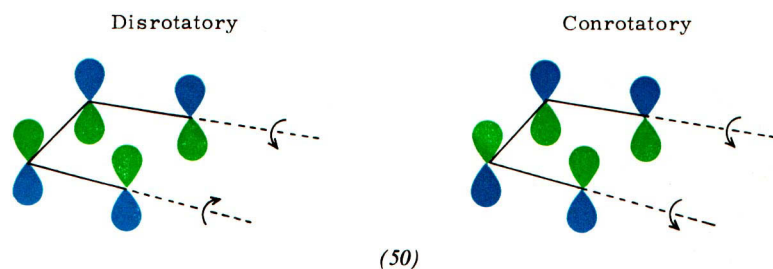
Figure 19. Correlation diagrams for the disrotatory and conrotatory conversion of cyclobutenes to butadienes.

relation diagram and its initial slope is an important indication of whether the process is symmetry-allowed or forbidden. Consider the disrotatory and conrotatory motions as they affect χ_2 in butadiene (50).

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 reacting system, but the analysis is often less simple than it is in the case of the butadiene \rightarrow 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.

The general rules for electrocyclic reactions are very easily derivable from the nodal properties of polyenes and polyenyl ions: the thermal electrocyclic reactions of a k π electron system will be disrotatory for $k = 4q+2$, conrotatory for $k = 4q$ ($q = 0, 1, 2, \dots$); in the first excited state these relationships are reversed. Some of the consequences of the rules are summarized in Figure 20.

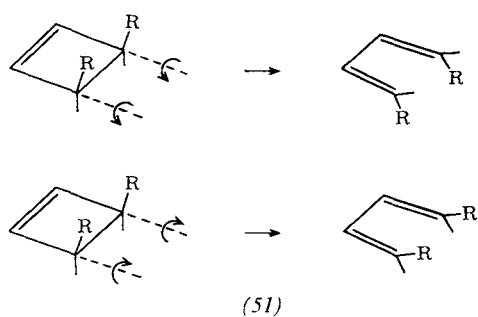
We turn next to a consideration of secondary factors which influence the actual composition of the products of an electrocyclic reaction. The first is steric control. For every reaction there are two conrotatory and two disrotatory motions which may or may not be distinguishable. Thus, the two conrotatory modes of opening



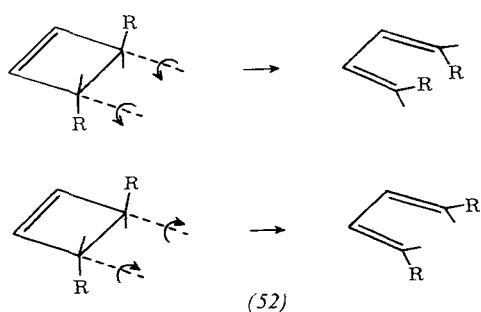
Reaction	Ground State	Excited State
	Conrotatory	Disrotatory
	Disrotatory	Conrotatory
	Conrotatory	Disrotatory
	Disrotatory	Conrotatory
	Conrotatory	Disrotatory
	Conrotatory	Disrotatory
	Disrotatory	Conrotatory

Figure 20. Conrotatory and disrotatory electrocyclic reactions.

of a *cis*-dimethylcyclobutene are enantiomeric and lead to the same product, *cis,trans*-1,4-dimethylbutadiene (51).



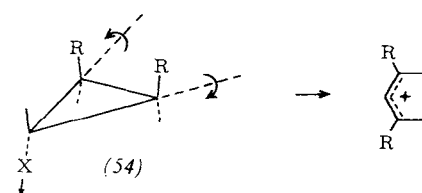
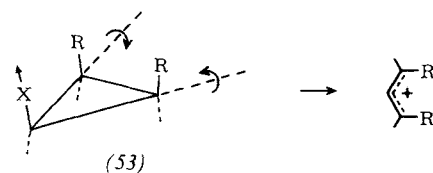
The two conrotatory motions for a *trans*-dimethylcyclobutene lead to two different isomers: *cis,cis*- and *trans,trans*-1,4-dimethylbutadiene (52). In fact, the *trans,trans* product is found exclusively^[13]; we attri-



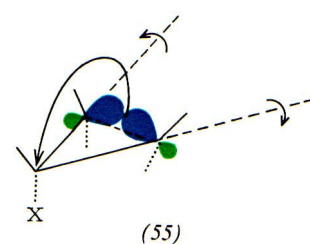
[13] R. E. K. Winter, *Tetrahedron Letters* 1965, 1207.

bute this to the unfavorable steric situation in the transition state leading to the *cis,cis* product.

A most interesting subsidiary question in connection with the electrocyclic opening of a cyclopropyl cation to an allyl cation was first posed to us by C. H. DePuy: assuming that departure of a leaving group from a cyclopropane ring, and the bond-breaking electrocyclic reaction to give an allyl cation, are concerted, could there be a difference between the two *a priori* possible disrotatory modes, defined in relation to the position of the leaving group? Extended Hückel calculations provided the initial answer, which may be summarized by saying that the substituents on the same side of the three-membered ring as the leaving group rotate towards one another (53), whereas those on the other side rotate apart (54).

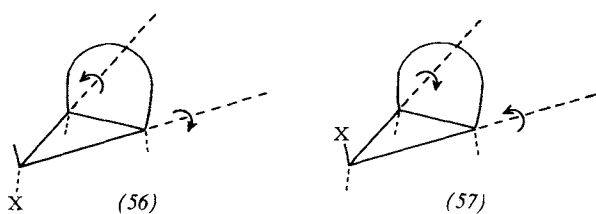


The result may be understood in qualitative terms when it is realized that as the 2,3 bond is broken by disrotatory outward rotation (55), the electron density of that bond, which originally was more or less in the plane of the cyclopropane ring, shifts above the plane. It is then available for backside displacement of the leaving group – in other words, the reaction is a normal S_N2 displacement of the group X by the electrons of the backbone σ bond of the cyclopropane ring.



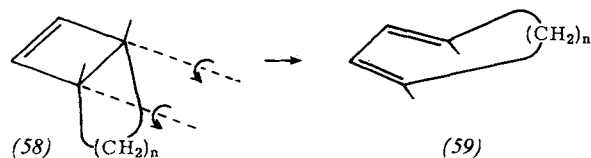
Several corollaries of these conclusions follow. If R in (53) or (54) is some bulky group then we should expect for steric reasons a faster solvolysis for compound (54). On the other hand, when *cis* positions are linked by a short methylene chain, we should expect the opening of a compound such as (56) with leaving group *anti*

to the ring to be severely disfavored, since the resulting rotation would lead to a *trans,trans*-allyl cation in a small ring. We should expect a facile opening only for a *syn* leaving group, as in (57).



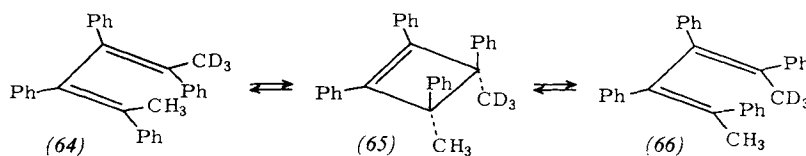
5.1. Electrocyclic Reactions Exemplified

The conrotatory electrocyclic change of a cyclobutene to a butadiene is a very well-known process. Its stereochemistry was established some ten years ago [14] and its scope and energetics have been very carefully studied [15]. 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 conrotatory displacement is symmetry-allowed, it follows that



a 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 beau-



tifully reflected in the temperatures at which the half-life of compound (58) is about 2 hours [16] as *n* is varied:

<i>n</i>	1	2	3	4	5	6
T(°C)	<100	195	>380	350	335	180

[14] E. Vogel, *Liebigs Ann. Chem.* 615, 14 (1958); R. Criegee and K. Noll, *ibid.* 627, 1 (1959).

[15] R. Criegee, D. Seebach, R. E. Winter, B. Börretzen, and H.-A. Brune, *Chem. Ber.* 98, 2339 (1965) and references therein; G. R. Branton, H. M. Frey, and R. F. Skinner, *Trans. Faraday Soc.* 62, 1546 (1966) and references therein. H. M. Frey and R. Walsh, *Chem. Rev.* 69, 103 (1969).

[16] R. Criegee and G. Bolz, unpublished work; D. Seebach, personal communication. The value for *n* = 1 is estimated from J. I. Brauman, L. E. Ellis, and E. E. van Tamelen, *J. Amer. chem. Soc.* 88, 846 (1966). A more detailed study of the case (58), *n* = 4, has been reported recently: J. J. Bloomfield, J. S. McConaghy, jr., and A. G. Hortmann, *Tetrahedron Letters*, 1969, 3723.

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

Molecules such as bicyclo[2.2.0]hexadiene and bicyclo[2.1.0]pentene clearly owe whatever stability they possess to the fact that the transformations, respectively to benzene and cyclopentadiene, are symmetry-forbidden.

Criegee and Reinhardt [17] have synthesized the laterally fused *cis*- and *trans*-cyclobutenes (60) – (63). These exhibited dramatically different pyrolytic stabilities [18]. In the substances with *anti* backbones, the symmetry-imposed conrotatory motion leads to *cis* double bonds in the six- or seven-membered rings and the electrocyclic cleavage takes place readily. By contrast, the

	E_a (kcal/mole)	$k = 10^{-4}$ at °C
(60)	42	261
(61)	29	87
(62)	45	273
(63)	27	109

symmetry-allowed processes with the *syn* isomers would give substances containing a *trans* double bond in a six- or a seven-membered ring. Consequently, the

transformation occurs only at extreme temperatures; it might well proceed by a non-concerted mechanism.

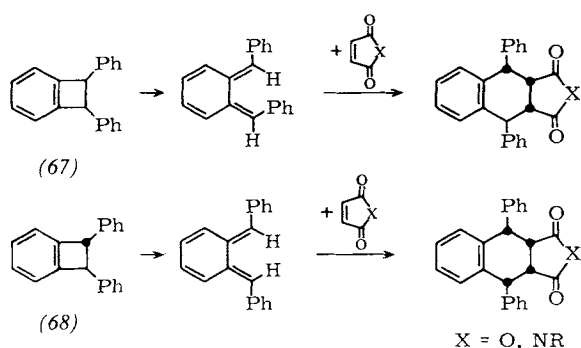
The highly substituted butadienes (64) and (66) have been studied in a most ingenious and amusing experiment [19]. These substances are equilibrated through the intermediacy of the cyclobutene (65). After fifty-one days at 124 °C, each cyclobutene molecule had faultlessly undergone 2.6×10^6 conrotatory openings, and a disrotatory mistake was yet to appear.

[17] R. Criegee and H. G. Reinhardt, *Chem. Ber.* 101, 102 (1968).

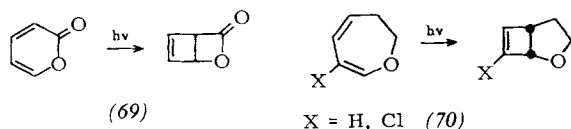
[18] Indications of a similar preference in laterally fused nine-membered rings had been found earlier: K. G. Untch and D. J. Martin, *J. Amer. chem. Soc.* 87, 4501 (1965).

[19] G. A. Doorakian and H. H. Freedman, *J. Amer. chem. Soc.* 90, 5310, 6896 (1968).

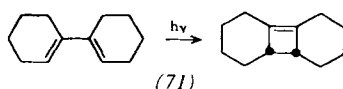
Some fascinating transformations of the *cis*- and *trans*-benzocyclobutenes (67) and (68) are readily explicable as electrocyclic reactions followed by Diels-Alder additions [20].



There are numerous examples of photochemical cyclobutene-butadiene interconversions. In the great majority of cases the diene is part of a cyclic system and is thus constrained to undergo the symmetry-allowed disrotatory process. Some typical examples are the reactions (69) and (70) [21, 22].

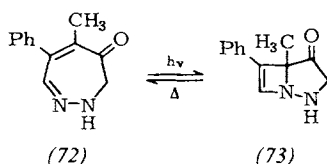


One case with greater stereochemical freedom (71) has been observed [23] and fits our expectations.



Recently it has been confirmed that *trans,trans*-2,4-hexadiene undergoes photochemical cyclization to *cis*-dimethylcyclobutene [24]; the case is of special interest in that geometric constraints are absent.

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



[20] R. Huisgen and H. Seidel, *Tetrahedron Letters* 1964, 3381; G. Quinkert, K. Opitz, W. W. Wiersdorff, and M. Finke, *ibid.* 1965, 3009.

[21] E. J. Corey and J. Streith, *J. Amer. chem. Soc.* 86, 950 (1964).

[22] L. A. Paquette, J. H. Barrett, R. P. Spitz, and R. Pitcher, *J. Amer. chem. Soc.* 87, 3417 (1965).

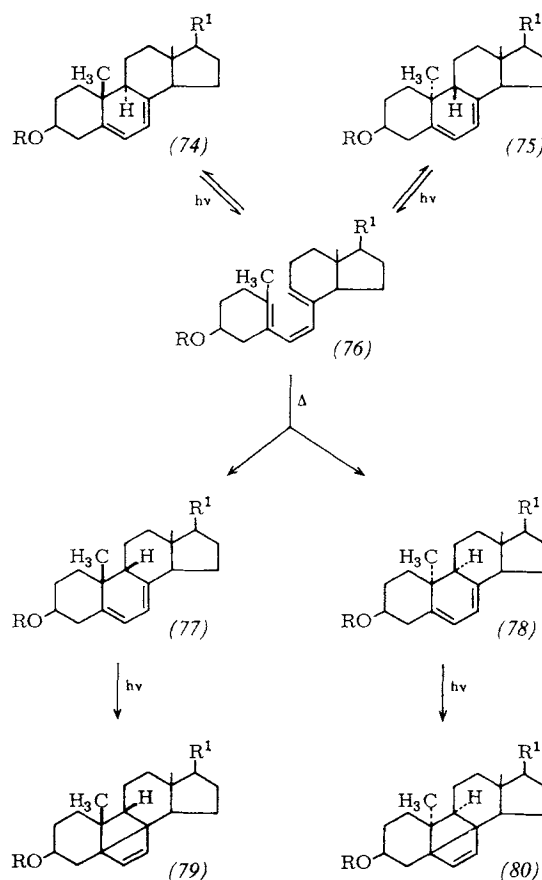
[23] W. G. Dauben, R. G. Cargill, R. M. Coates, and J. Saltiel, *J. Amer. chem. Soc.* 88, 2742 (1966); K. J. Crowley, *Tetrahedron* 21, 1001 (1965).

[24] R. Srinivasan, *J. Amer. chem. Soc.* 90, 4498 (1968).

starting compound [25]. The reversibility is easily understood once it is realized that direct *cis*→*trans* interconversion, an impossible process in fused carbocyclic systems, is simply an inversion at the nitrogen atom in (73).

The symmetry-allowed photochemical conrotatory cyclization of *cis*-hexatrienes, and the reverse reaction, were first recognized in studies in the vitamin D field. The conversions (74)–(80) – all symmetry-allowed – were established in an extensive series of elegant investigations [26].

Of particular interest is the fact that the cyclohexadienes (77) and (78), prevented by insurmountable geometrical restraints from undergoing symmetry-allowed electrocyclic cleavage, are photoisomerized to the cyclobutenes (79) and (80), in an alternative symmetry-allowed process.



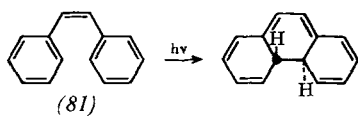
A further example of the photochemical cyclohexadiene→hexatriene reaction has recently been studied [27].

A related reaction presumably also takes place in the photocyclization of *cis*-stilbenes (81) and similar com-

[25] W. J. Theuer and J. A. Moore, *Chem. Commun.* 1965, 468.

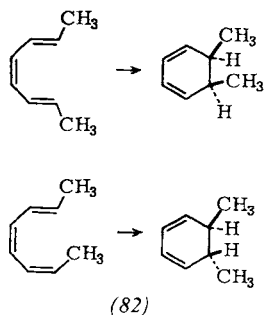
[26] E. Havinga, R. J. de Kock, and M. P. Rappold, *Tetrahedron* 11, 278 (1960); E. Havinga and J. L. M. A. Schlattmann, *ibid.* 16, 146 (1961); G. M. Sanders and E. Havinga, *Rec. Trav. chim.* 83, 665 (1964); H. H. Inhoffen and K. Irmischer, *Fortschr. Chem. org. Naturstoffe* 17, 70 (1959); H. H. Inhoffen, *Angew. Chem.* 72, 875 (1960); B. Lythgoe, *Proc. chem. Soc.* 1959, 141; W. G. Dauben and G. J. Fonken, *J. Amer. chem. Soc.* 81, 4060 (1959).

[27] P. Courtot and R. Rumin, *Tetrahedron Letters* 1968, 1091.

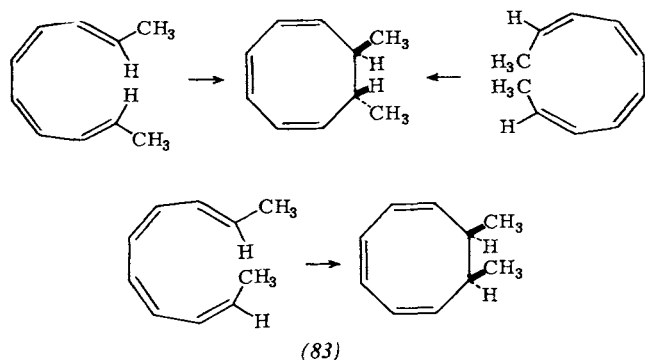


pounds [28], though the stereochemistry of the product has not been definitely established.

The earlier indications that the *thermal* cyclization of trienes was disrotatory [26] were confirmed by the study of simple model compounds (82) [29].



The electrocyclic closure (83) of a *cis,cis*-octatetraene should be thermally conrotatory, photochemically disrotatory. Though any conformation of a *cis,cis*-octatetraene is far from planarity, the nodal patterns in the orbitals are preserved. The predicted stereochemical course of the thermal reaction has been confirmed recently [30].



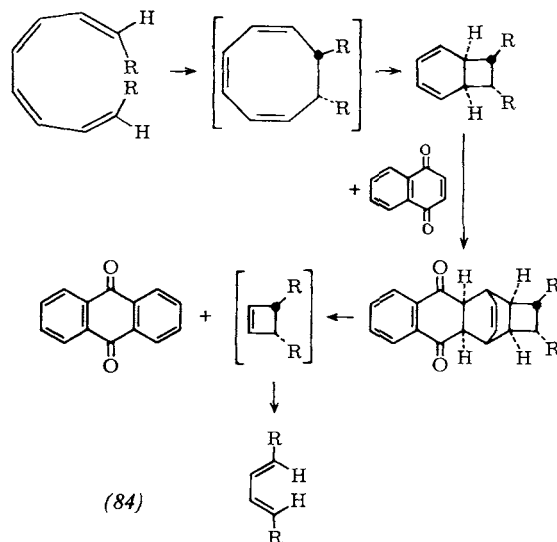
Some previous experiments can also be interpreted accordingly. Thus, in reactions (84) explored by Meister [31] the following sequence of symmetry-allowed changes can be adduced: an 8-electron conrotatory electrocyclic reaction, a 6-electron disrotatory reaction, a [4+2] cycloaddition, a reversion of the same, and a 4-electron conrotatory electrocyclic reaction.

[28] K. A. Muszkat and E. Fisher, *J. chem. Soc. B*, 1967, 662; F. B. Mallory, C. S. Wood, and J. T. Gordon, *J. Amer. chem. Soc.* 86, 3094 (1964). The subject has been recently reviewed by M. Scholz, F. Dietz, and M. Möhlstadt, *Z. Chem.* 7, 329 (1967).

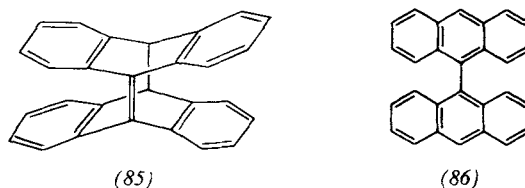
[29] E. Vogel, W. Grimme, and E. Dinné, *Tetrahedron Letters* 1965, 391; E. N. Marvell, G. Caple, and B. Schatz, *ibid.* 1965, 385; D. S. Glass, J. W. H. Watthey, and S. Winstein, *ibid.* 1965, 377.

[30] R. Huisgen, A. Dahmen, and H. Huber, *J. Amer. chem. Soc.* 89, 7130 (1967); cf. also E. N. Marvell and J. Seubert, *ibid.* 89, 3377 (1967).

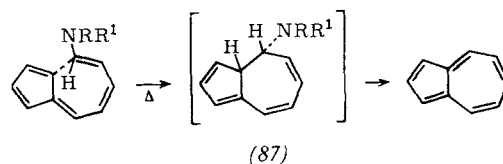
[31] H. Meister, *Chem. Ber.* 96, 1688 (1963).



The preparation of the fantastic hydrocarbon (85) by Greene [32] presents a situation of great interest, related to the octatetraene→cyclooctatriene electrocyclic conversion. Undoubtedly, the substance would suffer instantaneous transformation to its isomer 9,9'-bianthryl (86) – in fact, $t_{1/2} \approx 30$ minutes at 80 °C – were it 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 ten-electron electrocyclic reaction may have been realized in the Ziegler-Hafner synthesis of azulene [33]. The crucial cyclization step is very probably a disrotatory electrocyclic reaction (87).

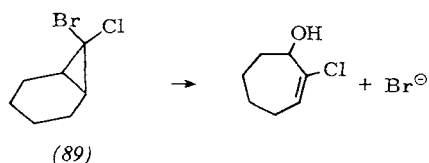
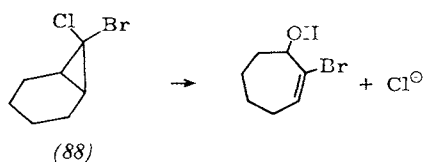


There were some previous indications in the literature that the opening of cyclopropyl cations to allyl cations is a stereospecific process [34]. For instance, Skell and Sandler observed that the two epimers (88) and (89)

[32] N. M. Weinshenker and F. D. Greene, *J. Amer. chem. Soc.* 90, 506 (1968).

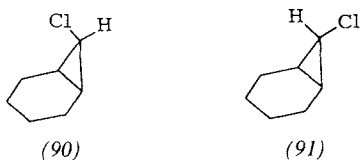
[33] K. Ziegler and K. Hafner, *Angew. Chem.* 67, 301 (1955); K. Hafner, *ibid.* 67, 301 (1955).

[34] (a) P. S. Skell and S. R. Sandler, *J. Amer. chem. Soc.* 80, 2024 (1958); (b) E. E. Schweizer and W. E. Parham, *ibid.* 82, 4085 (1960); (c) R. Pettit, *ibid.* 82, 1972 (1960).

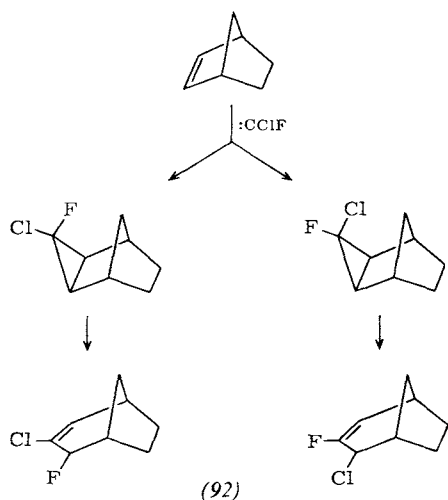


(structures not assigned) gave different solvolysis products. The hitherto mysterious phenomena are now readily explicable; the structures must be assigned as shown, since only loss of the *endo* halogen atoms can be concerted with the required disrotatory opening of the cyclopropane rings.

The first clear confirmations of our predictions for the electrocyclic opening were obtained in 1965. Whereas (90) undergoes solvolysis readily at 125 °C, its epimer (91) is recovered unchanged after prolonged treatment with acetic acid at 210 °C [35].



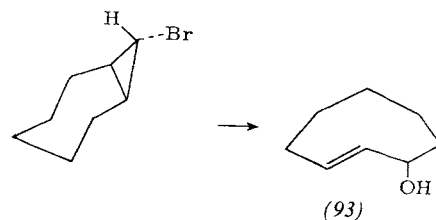
A detailed study of all methyl-substituted cyclopropyl tosylates clearly showed the steric effect of methyl groups forced against each other by the stereoelectronic factor [36].



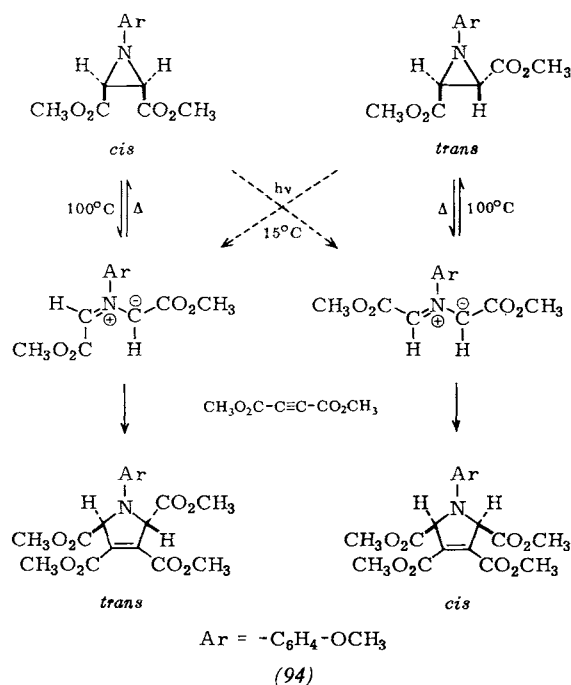
[35] S. F. Cristol, R. M. Segueira, and C. H. DePuy, *J. Amer. chem. Soc.* 87, 4007 (1965). Similar results were communicated to us by W. Kirmse. Cf. also the behavior on pyrolysis of the closely related chlorobicyclo[3.1.0]hexanes: M. S. Baird and C. B. Reese, *Tetrahedron Letters* 1967, 1379.

[36] P. v. R. Schleyer, G. W. Van Dine, U. Schöllkopf, and J. Paust, *J. Amer. chem. Soc.* 88, 2868 (1966); U. Schöllkopf, *Angew. Chem.* 80, 603 (1968); *Angew. Chem. internat. Edit.* 7, 588 (1968).

Since then, numerous further confirmations have appeared. We mention here only two of these. *Ghosez* and co-workers [37] observed the reactions (92), and *Whitham* has shown that solvolysis of *exo*-8-bromobicyclo[5.1.0]octane gives the expected *trans*-cyclooctenol (93) [38].



The electrocyclic cleavage of the cyclopropyl anion has not been tested directly in the parent case, but an iso-electronic example, drawn from aziridine chemistry, provides a striking confirmation of the conservation of orbital symmetry. The beautiful observations of *Huisgen*, *Scheer*, and *Huber* [39] are summarized in the diagram (94).



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

The cyclization of pentadienyl cations to cyclopentenyl ions is a reaction extensively studied by *Deno* and by

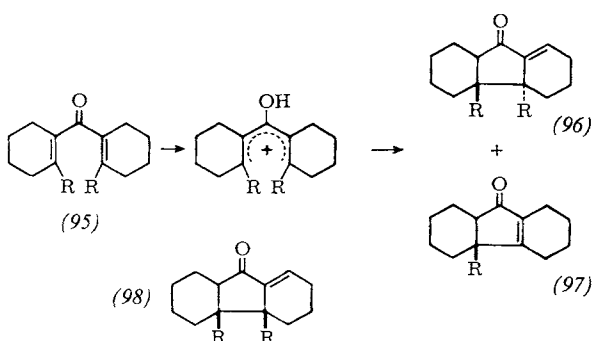
[37] L. Ghosez, G. Slinckx, M. Glineur, P. Hoet, and P. Laroche, *Tetrahedron Letters* 1967, 2773. Related reactions with HCl and HBr are also observed: C. W. Jefford, E. Huang Yen, and R. Medary, *ibid.* 1966, 6317.

[38] G. H. Whitham and M. Wright, *Chem. Commun.* 1967, 294.

[39] R. Huisgen, W. Scheer, and H. Huber, *J. Amer. chem. Soc.* 89, 1753 (1967).

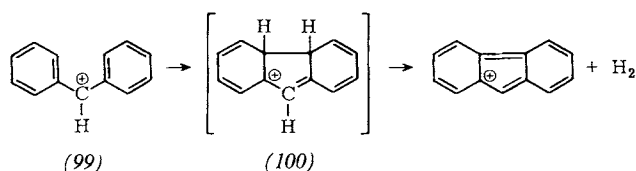
Sorensen^[40]. However, the nature of the sulfuric acid medium predominantly used in these studies precludes elucidation of the stereochemistry of the reaction; hydrogen and methyl shifts intervene before product isolation. Further, it is now clear that the well-known Nazarov reaction^[41] involves an electrocyclic reaction within a pentadienyl cation; again, no information about the stereochemistry of the change was forthcoming from the very extensive early work.

The stereochemistry of the reaction has now been established in recent studies at Harvard^[42]. Treatment of dicyclohexenyl ketone (95), R = H, with phosphoric



acid affords two ketones (96), R = H, and (97), R = H. Similarly, the substituted ketone (95), R = Me, yields (96), R = Me; in this case the process is not complicated by concomitant formation of a stereochemically uninformative product of type (97). Thus, the predicted conrotatory 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 excited state reactions of cations arises in mass-spectrometric studies. Johnstone and Ward^[43] observed that the diphenylmethyl cation (99), generated mass spectrometrically, cyclizes to a hydrofluorene species which loses two hydrogen atoms in a single step, and is therefore very



probably the *cis* ion (100) – the expected product of the symmetry-allowed electrocyclization of the first excited state of the cation (99). By contrast, the radical

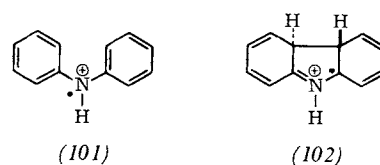
[40] N. C. Deno, C. V. Pittman, jr., and J. O. Turner, *J. Amer. chem. Soc.* 87, 2153 (1965); T. S. Sorensen, *Canad. J. Chem.* 42, 2768 (1964); 43, 2744 (1965); *J. Amer. chem. Soc.* 89, 3782, 3794 (1967).

[41] I. N. Nazarov and I. I. Zaretskaya, *Zh. Obsh. Khim.* 27, 693 (1957) and references therein.

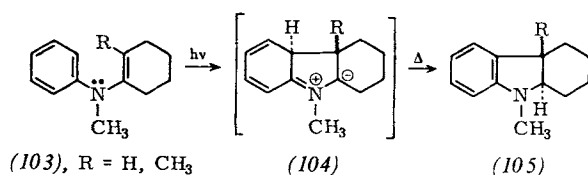
[42] R. Lehr, D. Kurland, and R. B. Woodward, unpublished observations. Cf. Dorothy Kurland, Dissertation, Harvard (1967); Roland Lehr, Dissertation, Harvard (1968).

[43] R. A. W. Johnstone and S. D. Ward, *J. chem. Soc. C*, 1968, 1805. However, cf. M. J. Bishop and I. Fleming, *ibid.* 1969, 1712.

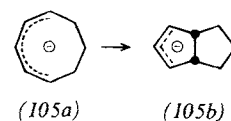
cation (101), cyclizes to a hydrocarbazol species which loses hydrogen atoms one at a time, and is thus probably the *trans* ion (102) – again the result of the symmetry-allowed excited state process.



Chapman^[44] has observed photochemical cyclizations of the amines (103). These are isoelectronic with pentadienyl anion, and their excited state closure should take a conrotatory course. The initially formed inter-



mediate (104) apparently returns to the ground state and undergoes a hydrogen shift (a symmetry-allowed suprafacial [1,4] anionic shift – see Section 7) leading to the stable final product (105).



Very recently, the first example of the electrocyclic closure of a simple cyclopentadienyl anion has been observed [(105a) → (105b)]^[44a].

Winstein has studied an exceptionally interesting system in which nine- and ten-electron electrocyclic processes are operative^[45]. When one electron is added to *cis*-bicyclo[6.1.0]nona-2,4,6-triene (106), an ion-radical (107) is produced, clearly with symmetry-allowed



disrotatory geometrical displacements. Moreover, yet another electron can be added, to give a ten-electron doubly charged anion. In spectacular contrast^[46], addition of an electron to the isomeric *trans*-triene (108) is not accompanied by delocalization of the cyclopro-

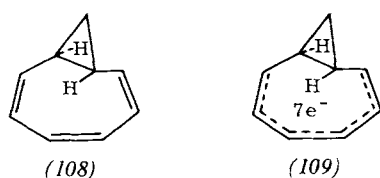
[44] O. L. Chapman and G. L. Eian, *J. Amer. chem. Soc.* 90, 5329 (1968).

[44a] R. B. Bates and D. A. McCombs, *Tetrahedron Letters* 1969, 977.

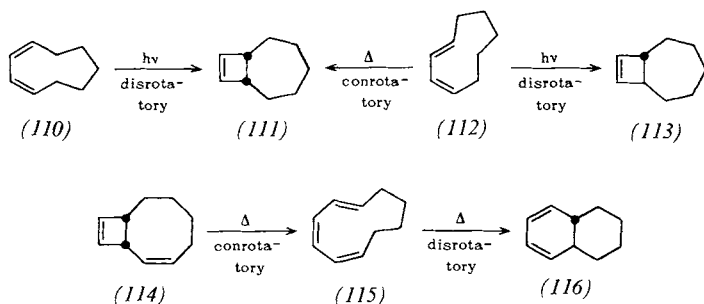
[45] R. Rieke, M. Ogliaruso, R. McClung, and S. Winstein, *J. Amer. chem. Soc.* 84, 4729 (1966); cf. also T. J. Katz and C. Talcott, *ibid.* 88, 4732 (1966).

[46] G. Moshuk, G. Petrowski, and S. Winstein, *J. Amer. chem. Soc.* 90, 2179 (1968).

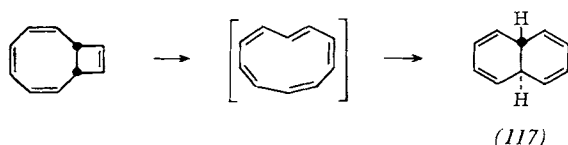
pane electrons. In this case, the steric restraints present do not permit disrotatory displacements, and the seven-electron ion-radical (109) is produced.



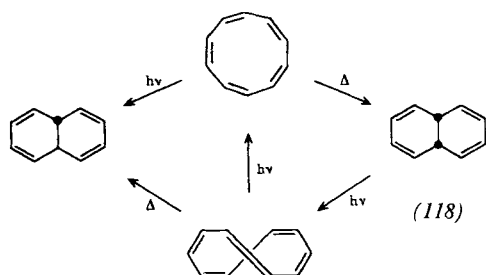
The congeries of electrocyclic reactions (110)–(116) was studied by *Fonken* [47], who correctly assumed, but did not observe, the intermediacy of (115) in the transformation of (114) into (116). In an independent investigation by *Radlick* [48] this course of events has been rigorously established.



A similar sequence of electrocyclic reactions is provided by the pyrolysis of bicyclo[6.2.0]deca-2,4,6,9-tetraene to *trans*-9,10-dihydronaphthalene (117) [49].



Trans-9,10-dihydronaphthalene is reported to be converted photochemically to a cyclodecapentaene (at -190°C) which reverts thermally to the *cis*-9,10-dihydronaphthalene (118) [50]; in more recent studies the



[47] *G. J. Fonken*, personal communication; *K. M. Schumate* and *G. J. Fonken*, *J. Amer. chem. Soc.* 87, 3996 (1965); 88, 1073 (1966).

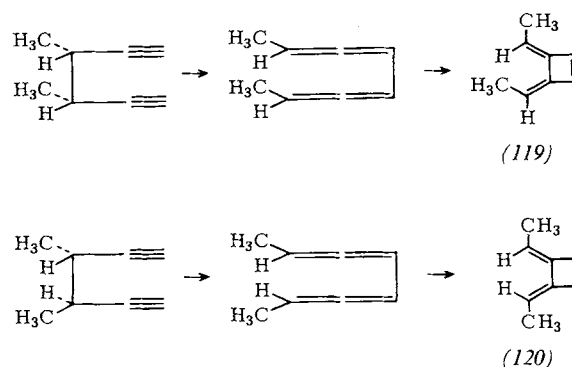
[48] *P. Radlick* and *W. Fenical*, *Tetrahedron Letters* 1967, 4901.

[49] *S. Masamune*, *C. G. Chin*, *K. Hojo*, and *R. T. Seidner*, *J. Amer. chem. Soc.* 89, 4804 (1967).

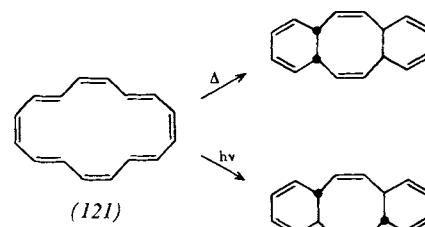
[50] *E. E. van Tamelen* and *T. L. Burkoth*, *J. Amer. chem. Soc.* 89, 151 (1967). Related cases were studied by *R. C. Cookson*, *J. Hudec*, and *J. Marsden*, *Chem. Ind.* 1961, 21, and by *E. Vogel*, *W. Meckel*, and *W. Grimme*, *Angew. Chem.* 76, 786 (1964); *Angew. Chem. internat. Edit.* 3, 643 (1964).

relationships shown in the diagram have been suggested [50a].

1,5-Alkadiynes undergo intramolecular rearrangement at elevated temperatures to give dimethylene cyclobutenes (119), (120). The observed stereospecificity [51] is

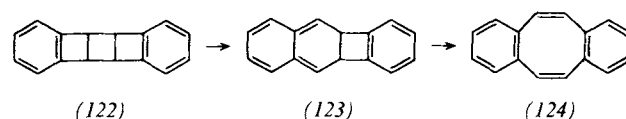


readily accounted for by the sequence of a symmetry-allowed [3,3] sigmatropic shift (see below, Section 7) and a four electron conrotatory electrocyclic reaction.



The recently synthesized [16]annulene isomerizes thermally and photochemically to two different isomers [52], the products of double disrotatory and double conrotatory closures, respectively.

Of very special interest is the recent discovery of metal catalysis of electrocyclic reactions. For example, the dibenzotricyclooctadiene (122) is reported to undergo



thermal isomerization to dibenzocyclooctatetraene (124) when heated at 180°C for 4–5 hours [53]. But at room temperature, in the presence of silver ions, the isomerization is complete in 10 seconds [54]. A forbidden disrotatory opening [(122)→(123)] is here obviously made allowed by the extra orbitals and electrons available from the complexing metal ion. A similar dramatic reversal of the rules for cycloaddition and cyclore-

[50a] *S. Masamune* and *R. T. Seidner*, *Chem. Commun.* 1969, 542.

[51] *W. D. Huntsman* and *H. J. Wristers*, *J. Amer. chem. Soc.* 89, 342 (1967).

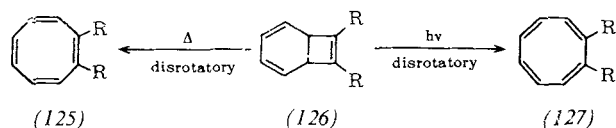
[52] *G. Schröder*, *W. Martin*, and *J. F. M. Oth*, *Angew. Chem.* 79, 861 (1967); *Angew. Chem. internat. Edit.* 6, 870 (1967).

[53] *M. Avram*, *D. Dinu*, *G. Mateescu*, and *C. D. Nenitzescu*, *Chem. Ber.* 93, 1789 (1960).

[54] *W. Merk* and *R. Pettit*, *J. Amer. chem. Soc.* 89, 4788 (1967).

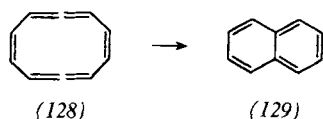
version reactions has been observed, and analyzed in terms of orbital symmetry conservation [55].

We now conclude our exemplification of electrocyclic reactions by alluding to two interesting, but as yet unrealized, possibilities. The valence tautomerism of cyclooctatetraene and bicyclo[4.2.0]octatriene is familiar [56]. The requisite disrotatory process may be achieved thermally by an opening of the six-membered ring of (126) or photochemically by cleavage of the cyclobutene ring. Since these electrocyclic changes might



be faster than bond switching in cyclooctatetraenes [57], it is possible that the alternatives might be experimentally observable.

The as yet unsynthesized cyclodeca-1,2,4,6,7,9-hexatriene (128) can exist in *meso* and *d,l* modifications. Both stereoisomers should be nearly strainless. The molecules are, of course, valence tautomers of naphthalene (129), and closure to naphthalene is formally an electrocyclic conversion of a hexatriene to a cyclohexadiene. The *meso* form (130) is in fact sterically



well-disposed for disrotatory closure to naphthalene; since that indeed is the symmetry-allowed electrocyclic mode, it would be expected that (130) would have a



very fragile grasp on existence. By contrast, the molecules of the *d,l* form [cf. (131)] have two interesting features. First, a model shows that an interesting conformational flipping can take place, without change of chirality. Second, the geometric circumstances are such that isomerization to naphthalene can be completed only by a symmetry-forbidden conrotatory closure. Consequently, the racemic compound might have reasonable thermal (but not photochemical) stability

[55] F. D. Mango and J. H. Schachtschneider, *J. Amer. chem. Soc.* 89, 2484 (1967); H. Hogeveen and H. C. Volger, *ibid.* 89, 2486 (1967).

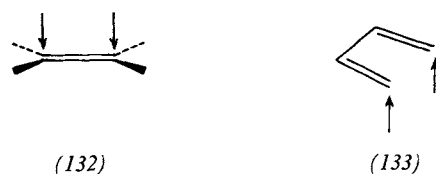
[56] E. Vogel, H. Kiefer, and W. R. Roth, *Angew. Chem.* 76, 432 (1964); *Angew. Chem. internat. Edit.* 3, 442 (1964); R. Huisgen and F. Mietzsch, *Angew. Chem.* 76, 36 (1964); *Angew. Chem. internat. Edit.* 3, 83 (1964).

[57] F. A. L. Anet, A. J. R. Bourn, and Y. S. Lin, *J. Amer. chem. Soc.* 86, 3576 (1964).

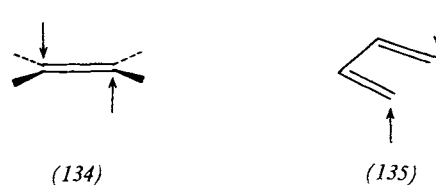
with respect to transformation into its aromatic isomer. By the same token, (131) is the product of the conrotatory cleavage of the 9,10 bond of the naphthalene molecule, and might well be among the products of photochemical transformation of the latter.

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 ethylenic (132) or cisoid diene system (133), formation of bonds in the senses indicated by the arrows takes place in a suprafacial manner.



A priori however, there are alternative, *antarafacial* processes, in which the newly formed or broken bonds lie on opposite faces of the reacting systems [58] [cf. (134) and (135)].



We shall use the terms *supra* and *antara* to designate these geometrical alternatives in making general allusions to reaction types, and the letters *s* and *a* as subscripts in defining particular reactions. Thus, the cycloadditions mentioned above are *supra,supra* reactions, and the Diels-Alder reaction is a [4_s+2_s] process [59].

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

In using the principle of orbital symmetry conservation to determine whether any cycloaddition is symme-

[58] The terms suprafacial and antarafacial were first used in our discussion of sigmatropic reactions; cf. ref. [3].

[59] We [Accounts of Chem. Res. 1, 17 (1968)] and others have earlier used *cis* and *trans* to designate the geometrical relationships here denominated *supra* and *antara*. However, the use of *cis* and *trans* as nomenclatural qualifiers is firmly established, and their employment in different senses — often of necessity, simultaneously — can be cumbersome and confusing, especially in discussing multicomponent combinations.

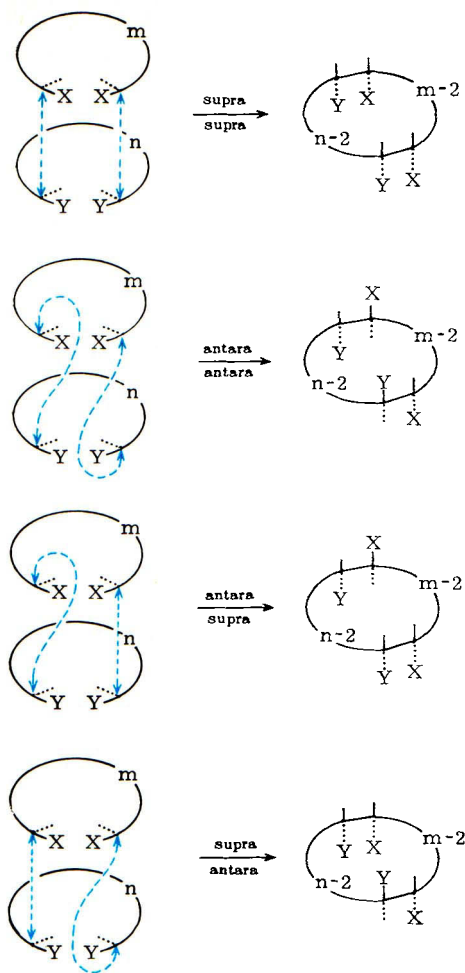


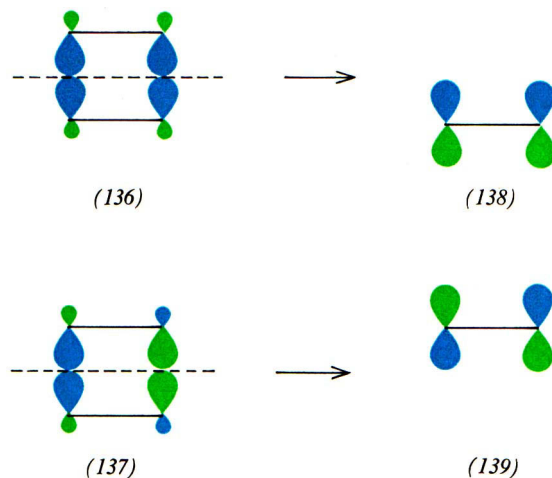
Figure 21. Stereochemical consequences of two-component cycloadditions. The diagrams are purely schematic, and do not reflect the actual geometry of the transition states, which of course differs markedly from case to case. Note that there are two possible *supra, supra* cases when m or $n > 2$, differing in the mode of approach of the reactants [*exo* and *endo* additions]. Similar circumstances obtain in the other cases. When the two reactants are identical the *supra, antara* and the *antara, supra* processes are indistinguishable.

try-allowed or forbidden, a complete analysis requires that all orbitals – bonding and antibonding – be considered. But a simplified procedure is often useful. First, all relevant reactant electrons are placed in fully delocalized bonding σ molecular orbitals of the *product* of the cycloaddition under examination. Then, if the electrons occupying the σ orbitals can be moved into bonding orbitals of the products of the cycloreversion when the σ bonds are broken with symmetry conservation, the reaction is symmetry-allowed. When the system is one lacking any molecular symmetry, the signs of the orbital lobes are determined by point-to-point transference from an analogous symmetrical system involving the same numbers of orbitals of the same types.

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

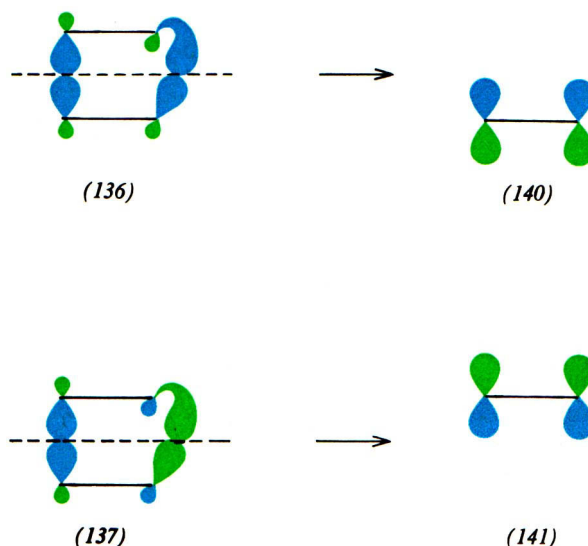


a) The $[2_s+2_s]$ process. When the σ bonds are cleaved, the two electrons in the orbital (136) can pass with symmetry conservation into a bonding orbital (138) of one ethylene molecule, but those in (137) can only enter an antibonding orbital (139) of the other ethylene.



The reaction is symmetry-forbidden.

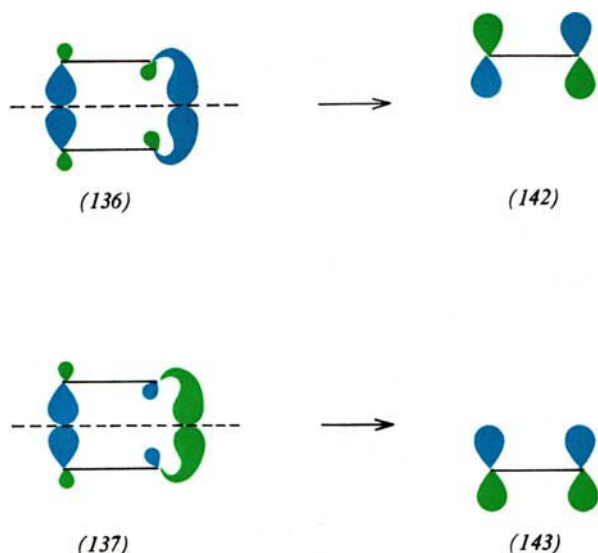
b) The $[2_s+2_a]$ process. When the σ bonds are cleaved, the two electrons in the orbital (136), now shown distorted in a purely formal manner, can pass with symmetry conservation into a bonding orbital (140) of one ethylene molecule, while those in (137) likewise pass into a bonding orbital (141) of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



The reaction is symmetry-allowed.

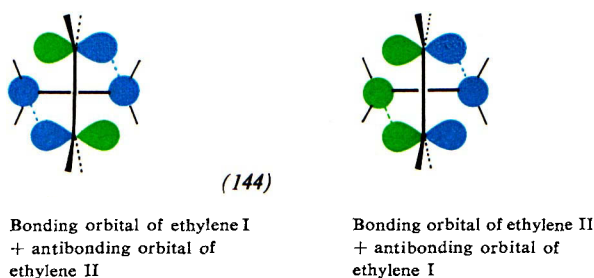
c) The $[2_a+2_a]$ process. When the σ bonds are cleaved, two electrons in the orbital (136), again, but different-

ly, distorted in a purely formal manner, can only enter an antibonding orbital (142) of one ethylene molecule, while those of (137) pass into a bonding orbital (143) of the other.

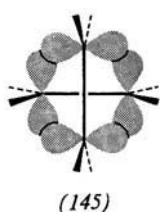


The reaction is symmetry-forbidden.

It will be noted that the analyses just completed reveal the existence of a concerted symmetry-allowed path for the combination of two ethylenic compounds to give a cyclobutane. What the simplified formal analysis does not render obvious is the actual geometry of approach for the allowed $[2_s+2_a]$ 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 $[2_s+2_a]$ reaction, it is clear that the ethylenic 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 $[2_s+2_a]$ reaction, using a two-fold axis of symmetry which passes through the midpoints of both of the ethylenic bonds. Similar circumstances obtain in the case of the $[2_a+2_a]$ reaction. In this case the geometry of approach is that shown in (145), and the reaction is



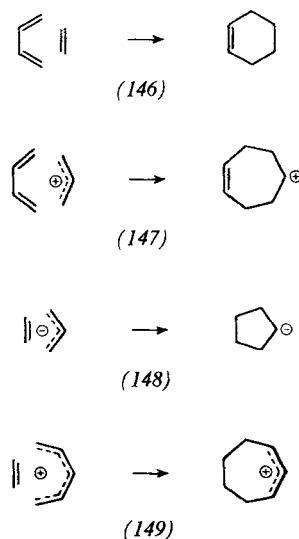
forbidden in the ground state, as deduced above, but allowed for the excited state (cf. Figure 22). A final point of much importance is that the principle of conservation of orbital symmetry is valid, whether or not a formal correlation diagram can be constructed. For example, no pertinent correlation diagrams can be drawn for the concerted $[4_s+2_a]$ and $[6_s+2_a]$ 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 m to an n -electron system the rules shown in Figure 22 must be observed for concerted processes (q is an integer = 1, 2, 3 . . .).

$m+n$	Allowed in Ground State Forbidden in Excited State	Allowed in Excited State Forbidden in Ground State
$4q$	m_s+n_a m_a+n_s	m_s+n_s m_a+n_a
$4q+2$	m_s+n_s m_a+n_a	m_s+n_a m_a+n_s

Figure 22. Selection rules for $[m+n]$ cycloadditions.

An important generalization is that these rules depend not on the total number of orbitals but on the number of electrons. Thus, the $[4+2]$ case may be achieved in each of the ways shown by formulae (146)–(149).



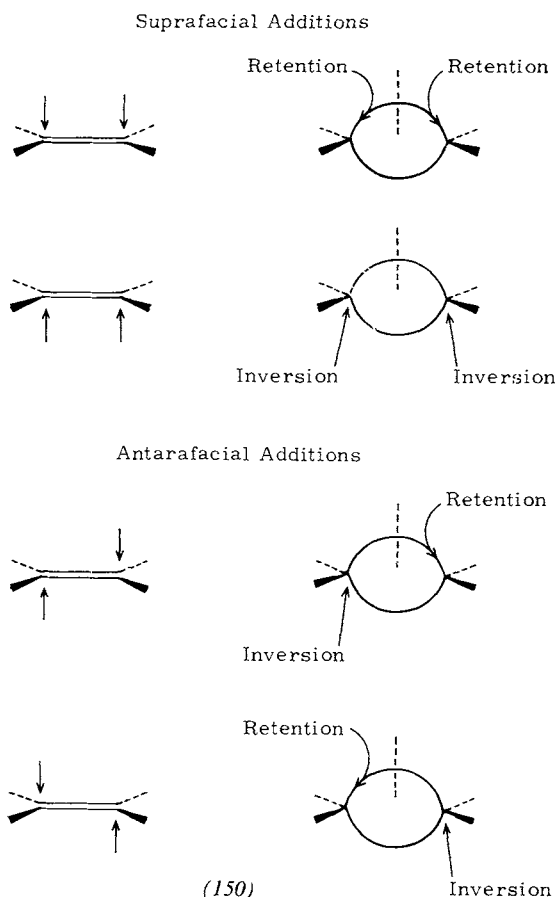
It should be noted also that *supra,antara* and *antara,antara* cycloadditions are not so unlikely as they might appear to be on simple steric grounds.

It remains to point out that σ bonds can act as components in cycloaddition reactions. In such cases, the following definitions are important:

a) A σ bond is considered to be involved in a cycloaddition reaction in a *supra* sense if configuration is retained, or inverted, at both of its termini in the course of reaction.

b) A σ bond is considered to be involved in a cycloaddition reaction in an *antara* sense if configuration is retained at one, and inverted at the other, terminus in the course of reaction.

The rationale underlying these important conventions will be apparent immediately upon consideration of additions to an ethylene molecule, regarded as containing two σ bonds (150).



c) We adopt the simple and useful device of denominating the type of orbital involved in a concerted reaction by a subscript preceding the number of electrons in the relevant orbital. Thus

$\sigma 2_a$ $\pi 4_s$ etc.

In order to clarify and exemplify these matters, it may be pointed out that the electrocyclic transformation of cyclobutenes to butadienes may be regarded formally as a cycloaddition of a σ bond to a π bond, in either of two equivalent ways.

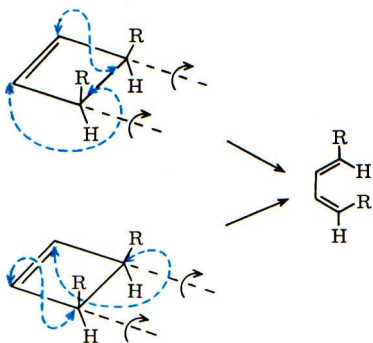


Figure 23. Electrocyclic conversion of cyclobutenes to butadienes as $[\sigma 2_s + \pi 2_a]$ cycloadditions.

a) As shown in Figure 23: *suprafacial* on the σ bond, *antarafacial* on the π bond, *i. e.* $[\sigma 2_s + \pi 2_a]$.

b) As shown in Figure 24: *antarafacial* on the σ bond, *suprafacial* on the π bond, *i. e.* $[\pi 2_s + \sigma 2_a]$.

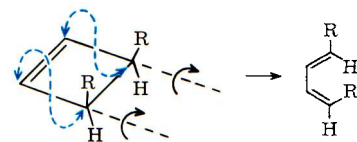
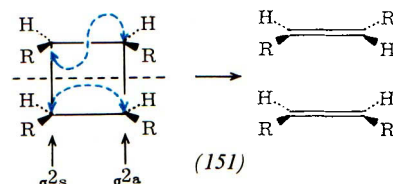


Figure 24. Electrocyclic conversion of cyclobutenes to butadienes as $[\pi 2_s + \sigma 2_a]$ cycloadditions.

It will be observed that whichever formal view is taken, the conrotatory processes represent symmetry-allowed cycloaddition reactions; by contrast, the disrotatory analogues must be regarded as $[\pi 2_s + \sigma 2_s]$ or $[\pi 2_a + \sigma 2_a]$ reactions, which are, of course, symmetry-forbidden in ground states.

As a final illustration we may now characterize the concerted scission of cyclobutane as a $[\sigma 2_s + \sigma 2_a]$ process (151).



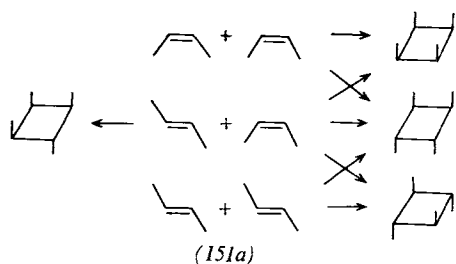
6.1. Cycloadditions and Cycloreversions Exemplified

The [2+2] cycloaddition is one of the most widely observed photochemical reactions, with more than one hundred examples quoted in a recent review^[60]. It is likely that many of these reactions are not concerted, probably as a consequence of the fact that competitive relaxation of a participant excited state occurs, 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^[61]; of course, it should be noted that *trans* fused products would result from concerted symmetry-allowed $[\pi 2_s + \pi 2_a]$ combinations of vibrationally excited ground-state molecules. Nevertheless, two striking examples of concerted symmetry-allowed photo-induced $[2_s + 2_s]$ processes have recently been observed. Thus, irradiation of the neat *cis*- and *trans*-2-butenes, separately and in admixture, gives the results shown in (151a)^[61a].

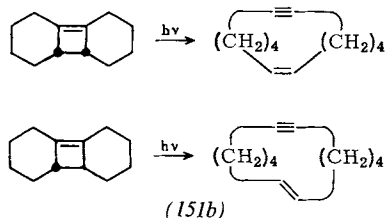
[60] R. N. Warrener and J. B. Bremner, *Rev. pure appl. Chem.* 16, 117 (1966). See also W. L. Dilling, *Chem. Rev.* 66, 373 (1966).

[61] E. J. Corey, J. D. Bass, R. LeMahieu, and R. B. Mitra, *J. Amer. chem. Soc.* 86, 5570 (1964); P. E. Eaton and K. Lin, *ibid.* 86, 2087 (1964); A. Cox, P. de Mayo, and R. W. Yip, *ibid.* 88, 1043 (1966); R. Robson, P. W. Grubb, and J. A. Barltrop, *J. chem. Soc.* 1964, 2153.

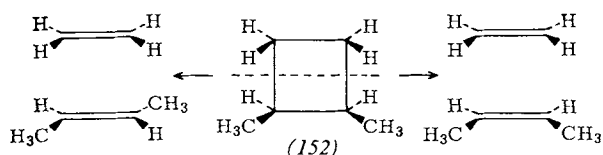
[61a] H. Yamazaki and R. J. Cvetanović, *J. Amer. chem. Soc.* 91, 520 (1969).



Further, a pretty example (151b) of the photochemical $[\sigma 2_s + \sigma 2_s]$ reaction has been discovered [61b].



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 [62]. Further, the fact that pyrolysis of *cis*- or *trans*-dimethylcyclobutane (152) yields a

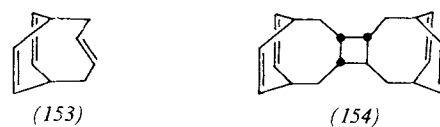


A beautiful example of the symmetry-allowed $[\pi 2_s + \pi 2_a]$ combination has been discovered by Kraft

[61b] J. Saliel and L.-S. Ng Lim, *J. Amer. chem. Soc.* 91, 5404 (1969).

[62] S. W. Benson and P. S. Nangia, *J. chem. Physics* 38, 18 (1963); see also the review by H. M. Frey in *V. Gold: Advances in Physical Organic Chemistry*. Academic Press, New York 1966, Vol. 4, p. 170.

[63] H. R. Gerberich and W. D. Walters, *J. Amer. chem. Soc.* 83, 3935, 4884 (1961).



and Koltzenburg [64]. The olefin (153) dimerizes spontaneously to (154).

Earlier observations [65] that *cis*, *trans*-cycloocta-1,5-diene (155) dimerizes spontaneously at room temperature to a bicyclobutane are less illuminating, since the stereochemistry of the product – now predictable as (156) – has not been established.



It is worthy of note that when a double bond is twisted about its axis – as it must be in (153) and (155) – the concomitant orbital twisting is such as distinctly to favor the $[\pi 2_s + \pi 2_a]$ process.

A further very 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 ethylene components. Consequently, we may predict that the optical-

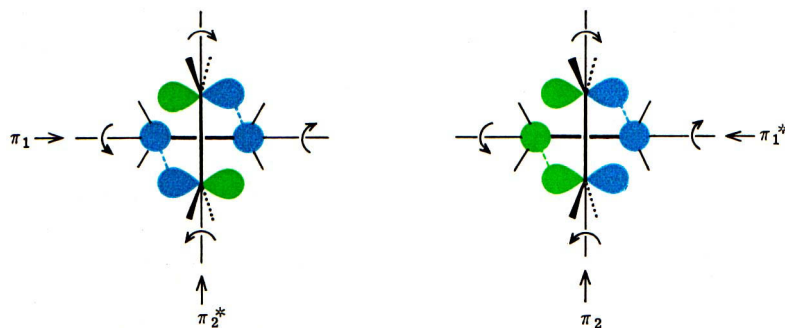


Figure 25. Combination of systems of opposite chirality in the $[\pi 2_s + \pi 2_a]$ cycloaddition of two ethylene molecules.

mixture of *cis*- and *trans*-butenes, among other products [63], has been adduced in support of the diradical mechanism. Nevertheless, if the cycloreversion is concerted, it must be of the type $[\sigma 2_s + \sigma 2_a]$, and the same stereochemical result would be observed.

ly active forms of the olefins (153) and (155) will dimerize less readily than the racemic substances.

Bicyclobutanes are produced on irradiation of some substituted butadienes [66] as well as butadiene itself [67]. The bicyclobutanes are remarkably stable, considering their strain energy (ca. 69 kcal/mole). The activation energy for isomerization to butadiene is 41 kcal/mole [68,69]. The temptation arises then to consider the rearrangement of bicyclobutane to butadiene

[64] K. Kraft and G. Koltzenburg, *Tetrahedron Letters*, 1967, 4357, 4723.

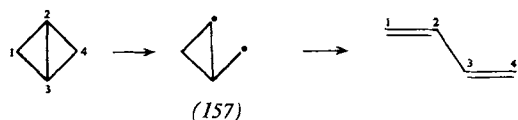
[65] K. Ziegler, H. Sauer, L. Bruns, H. Froitzheim-Kühlhorn, and J. Schneider, *Liebigs Ann. Chem.* 589, 122 (1954); K. Ziegler and H. Wilms, *ibid.* 567, 1 (1950); A. C. Cope, C. F. Howell, and A. Knowles, *J. Amer. chem. Soc.* 84, 3190 (1962).

[66] W. G. Dauben and W. T. Wipke, *Pure appl. Chem.* 9, 539 (1964), and references therein.

[67] R. Srinivasan, *J. Amer. chem. Soc.* 85, 4045 (1963).

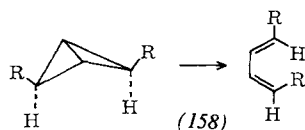
[68] H. M. Frey and I. D. R. Stevens, *Trans. Faraday Soc.* 61, 90 (1965).

[69] R. Srinivasan, A. A. Levi, and I. Haller, *J. phys. Chem.* 69, 1775 (1965).

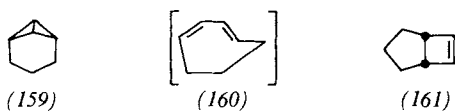


as a non-concerted process proceeding through a diradical intermediate (157).

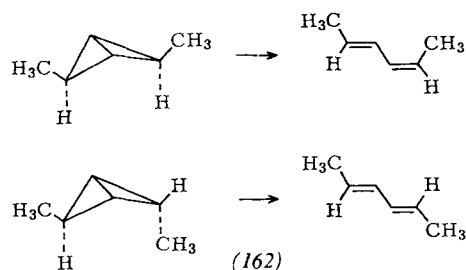
If, however, the reaction is a concerted one, it is clear that it must be a $[\sigma 2_s + \sigma 2_a]$ process, with the stereochemical consequences shown in (158) [70].



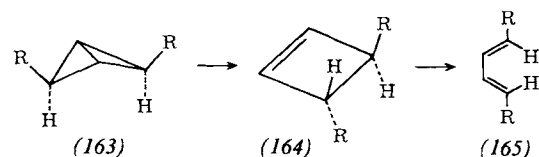
The evidence is now compelling that the reaction is in fact a concerted $[\sigma 2_s + \sigma 2_a]$ process. A first, indirect indication that such is the case, was provided by the observation that (159) is converted to (161) on pyrolysis [71]. The result is best accommodated by assuming the



intermediacy of (160), which closes in a conrotatory fashion to the observed product. The decisive experiment was recently reported by Closs and Pfeffer [72]. Their results are summarized in (162).



Remarkably, there exists in principle an alternative pathway relating bicyclobutane and butadiene, with precisely opposite stereochemical consequences. This route [(163) \rightarrow (164) \rightarrow (165)] entails the intermediacy of a cyclobutene, which then undergoes conrotatory cleavage to the product butadiene. Thermodynamically,



[70] Similar conclusions have been reached by Wiberg on the basis of semi-empirical MO calculations [K. B. Wiberg, *Tetrahedron* 24, 1083 (1968)].

[71] K. B. Wiberg and G. Szeimies, *Tetrahedron Letters*, 1968, 1235.

[72] G. L. Closs and P. E. Pfeffer, *J. Amer. chem. Soc.* 90, 2452 (1968).

ally, the sequence is feasible [73]. In formal terms, the change may be described as involving successive symmetry-allowed $[\sigma 2_s + \sigma 2_a]$ and $[\sigma 2_s + \pi 2_a]$ reactions. The possibility that special substitution patterns – perhaps operating through attendant simple steric effects – may bring this path to light should not be dismissed.

The reader may find it illuminating to verify for himself the relationships displayed in Figure 26, which presents the stereochemical pattern for all possible symmetry-allowed processes relating bicyclobutanes, cyclobutenes, and butadienes.

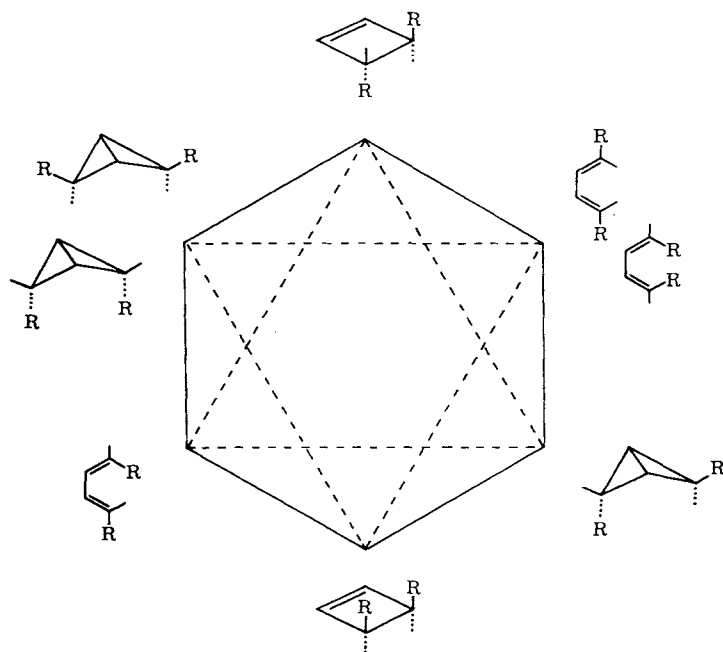


Figure 26. Symmetry-allowed processes relating bicyclobutanes, cyclobutenes, and butadienes. — Allowed ground state paths. --- Allowed excited state paths.

The number of known Diels-Alder reactions – the $[\pi 4_s + \pi 2_s]$ cycloadditions – is legion [74, 75]. Though a diradical mechanism has been advanced on numerous occasions [76], the overwhelming body of experimental facts is consistent only with a concerted mechanism [77].

There is a growing body of photochemical Diels-Alder reactions [78], but in most instances there is no evidence which provides information as to whether the reactions are concerted or not. However, it is very probable that concerted symmetry-allowed excited-state $[\pi 4 + \pi 2]$ processes are involved in the ubiquitous conversion of

[73] R. B. Turner, P. Goebel, W. von E. Doering, and J. F. Coburn, *jr.*, *Tetrahedron Letters* 1965, 997.

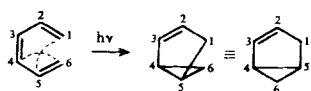
[74] R. Huisgen, R. Grashey, and J. Sauer in S. Patai: *The Chemistry of Alkenes*. Interscience, New York 1964, p. 739.

[75] A. Wassermann: *The Diels-Alder Reaction*. Elsevier, Amsterdam 1965.

[76] Most recently by S. W. Benson, *J. chem. Physics* 46, 4920 (1967).

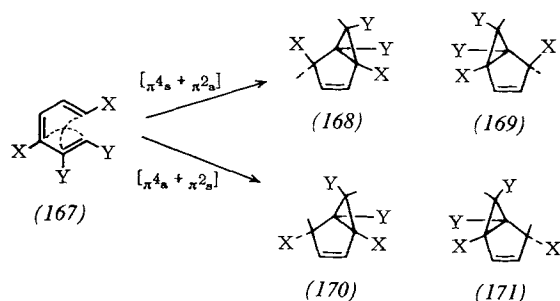
[77] R. B. Woodward and T. J. Katz, *Tetrahedron* 5, 70 (1959).

[78] For example, G. S. Hammond, N. J. Turro, and R. S. H. Liu, *J. org. Chem.* 28, 3297 (1963); G. S. Hammond and R. S. H. Liu, *J. Amer. chem. Soc.* 85, 477 (1963); D. Valentine, N. J. Turro, and G. S. Hammond, *ibid.* 86, 5202 (1964); R. S. H. Liu, N. J. Turro, and G. S. Hammond, *ibid.* 87, 3406 (1965); G. O. Schenck, S.-P. Mannsfeld, G. Schomburg, and C. H. Krauch, *Z. Naturforsch.* 19b, 18 (1964).

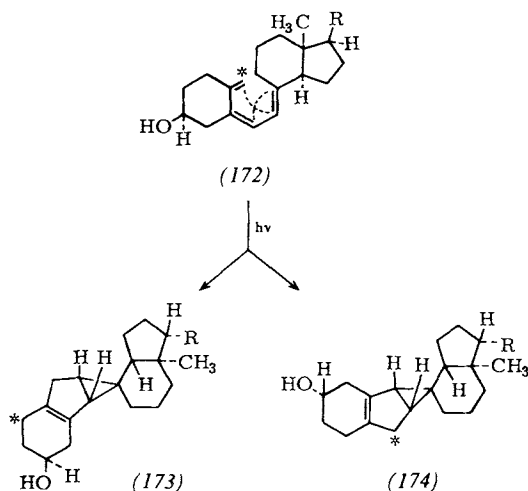


(166)

cis-hexatrienes (166) to bicyclo[3.1.0]hexenes [79]. If concerted, these reactions must be either $[\pi 4_s + \pi 2_a]$ or $[\pi 4_a + \pi 2_s]$ processes. Excluding the formation of a *trans* fused bicyclohexene, the stereochemical consequences of the allowed processes are seen from formulae (167)–(171).



No reaction involving a substance sufficiently extensively labeled as to provide a test of these conclusions has been studied. In vitamin D₂ (172), the top and bottom faces of the triene system are no longer equivalent, and the processes which lead in the general cases to en-



antiomers must in this instance afford different structures. In fact, irradiation of vitamin D₂ leads to two bicyclohexenes—suprasterol I (173) [80] and suprasterol II (174) [81]. These structures are precisely those which must result from concerted symmetry-allowed excited-state $[\pi 4_s + \pi 2_a]$ processes, but in the absence of fur-

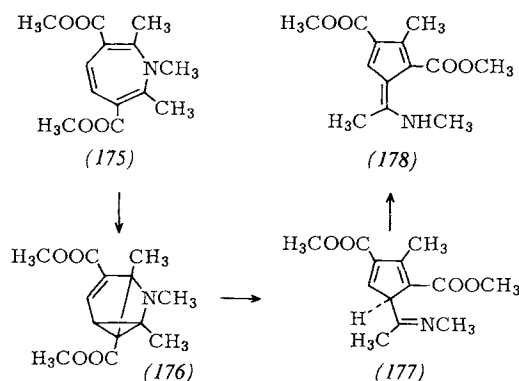
[79] J. Meinwald and P. H. Mazzocchi, *J. Amer. chem. Soc.* 88, 2850 (1966); J. Meinwald, A. Eckell, and K. L. Erickson, *ibid.* 87, 3532 (1965); H. Prinzbach and H. Hagemann, *Angew. Chem.* 76, 600 (1964); *Angew. Chem. internat. Edit.* 3, 653 (1964); H. Prinzbach and E. Druckrey, *Tetrahedron Letters* 1965, 2959; K. J. Crowley, *ibid.* 1965, 2863.

[80] W. G. Dauben, personal communication; W. G. Dauben, I. Bell, T. W. Hutton, G. F. Laws, A. Rheiner, and H. Urscheler, *J. Amer. chem. Soc.* 80, 4116 (1958).

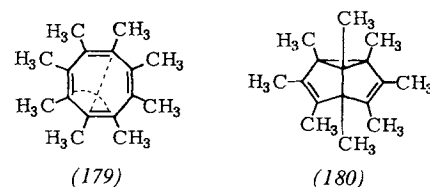
[81] W. G. Dauben and P. Baumann, *Tetrahedron Letters* 1961, 565; C. P. Saunderson and D. C. Hodgkin, *ibid.* 1961, 573.

ther labeling at the starred atoms it is not possible to discern whether the $\pi 4$ system participates in the reactions in a suprafacial manner.

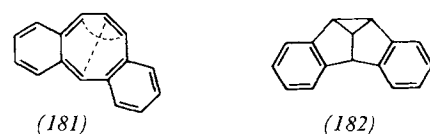
A proposed mechanism for the observed transformation of the azepine (175) into the fulvene (178) invokes the symmetry-allowed ground-state $[\pi 4_a + \pi 2_a]$ reaction (175) \rightarrow (176) [82].



At elevated temperatures, in the presence of base, octamethylcyclooctatrasne (179) is smoothly converted to octamethylsemibullvalene (180) [83]. It seems possi-



ble that the base serves merely to protect the reactant from alternative acid-catalyzed changes, and that the reaction is a simple symmetry-allowed $[\pi 4_a + \pi 2_a]$ intramolecular cycloaddition. Further, Pettit [84] has made observations which are best interpreted by assuming that dibenzo[*a,c*]cyclooctatetraene (181) undergoes spontaneous transformation to (182); the special points worthy of note in this case are that the $[\pi 4_a + \pi 2_a]$



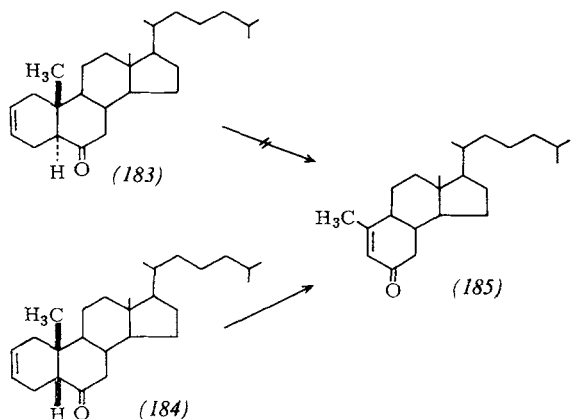
reaction is favored both by concomitant loss of *o*-quinoid character as reaction proceeds, and by deviation in (181) from normal cyclooctatetraene geometry, induced by the fused six-membered rings. The difficulty of the $-\pi 4_a + \pi 2_a$ process [84a] in the absence of favorable steric constraints is shown by the fact that the ketone (183) fails to undergo cycloreversion to butadiene and

[82] R. F. Childs, R. Grigg, and A. W. Johnson, *J. chem. Soc. C*, 1967, 201.

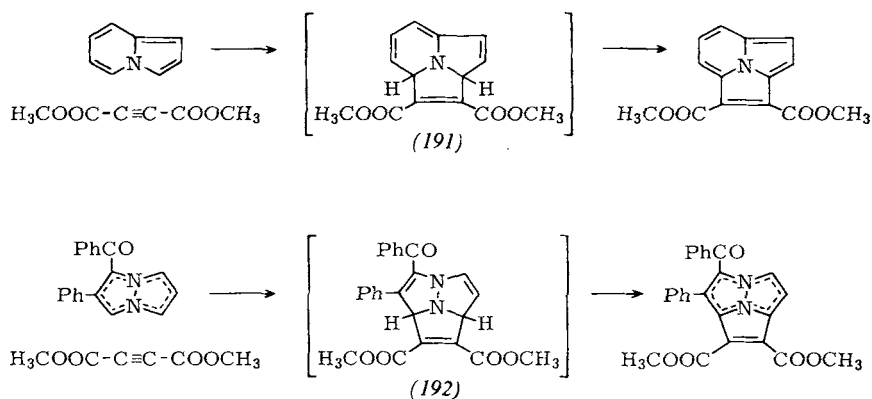
[83] R. Criegee and R. Askani, *Angew. Chem.* 80, 531 (1968); *Angew. Chem. internat. Edit.* 7, 537 (1968).

[84] G. F. Emerson, L. Watts, and R. Pettit, *J. Amer. chem. Soc.* 87, 131 (1965); W. Merk and R. Pettit, *ibid.* 89, 4787 (1967).

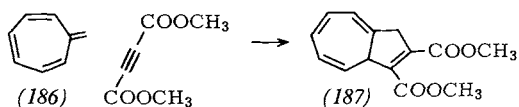
[84a] Here and in the sequel we use the device of placing a negative sign before the bracket whenever a reaction is characterized in terms of its products.



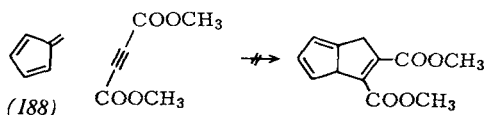
(185) even at 400 °C; the corresponding $-\left[\pi 4_s + \pi 2_s\right]$ reaction (184) \rightarrow (185) takes place readily^[85].



[4+4] Cycloadditions are well known^[86]. As yet, they have been encountered only in photochemical reactions, and no detailed stereochemical information is available.



[8+2] Cycloadditions have been relatively rarely observed. Heptafulvene (186) readily combines with dimethyl acetylenedicarboxylate^[87] to give (187), whereas fulvene (188) does not react in a similar sense (note that the $[\pi 6_s + \pi 2_s]$ combination is symmetry-forbidden). Similar reactions of calicenes have been observed^[88]. Hexaphenylpentalene (189) also combines

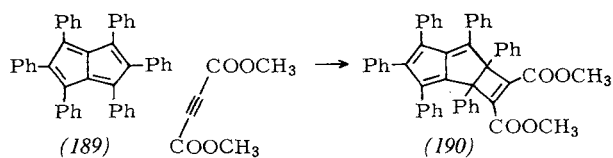


[85] H. R. Nace, personal communication.

[86] L. A. Paquette and G. Slomp, *J. Amer. chem. Soc.* 85, 765 (1963); P. de Mayo and R. W. Yip, *Proc. chem. Soc.* 1964, 84; D. E. Applequist and R. Searle, *J. Amer. chem. Soc.* 86, 1389 (1964); J. S. Bradshaw and G. S. Hammond, *ibid.* 85, 3953 (1963); K. Kraft and G. Koltzenburg, *Tetrahedron Letters* 1967, 4357.

[87] W. von E. Doering and D. W. Wiley, *Tetrahedron* 11, 183 (1960).

[88] H. Prinzbach, D. Seip, and G. Englert, *Liebigs Ann. Chem.* 698, 57 (1966); H. Prinzbach, D. Seip, L. Knothe, and W. Faisst, *ibid.* 698, 34 (1966).



with the acetylenic ester, producing an azulene by way of an adduct (190), as yet not isolated, which is the product of an [8+2] reaction^[89].

Two unusual [8+2] cycloadditions, discovered by Boekelheide^[90], are portrayed in (191) and (192).

[6+4] Cycloadditions were unknown until our enunciation of the principle of orbital symmetry conservation stimulated the search for them. The cases (193)–(198) are now known.

[6+6] Cycloadditions of presumed *p*-xylylene intermediates are known^[96], but no information is available about the detailed mechanism of the reactions. Irradiation of tropone in acidic solution gives a symmetrical dimer (199)^[97], which is the product to be expected from a concerted symmetry-allowed excited-state $[\pi 6_s + \pi 6_s]$ combination; the unusual experimental conditions, and the fact that other photoinduced dimerizations of tropone may proceed in a non-concerted fashion^[98] suggest caution in adopting the conclusion that the concerted process is in fact involved in the formation of (199).

[89] E. Le Goff, *J. Amer. chem. Soc.* 84, 3975 (1962).

[90] A. Galbraith, T. Small, R. A. Barnes, and V. Boekelheide, *J. Amer. chem. Soc.* 83, 453 (1961); V. Boekelheide and N. A. Fedoruk, *Proc. nat. Acad. Sci.* 55, 1385 (1966).

[91] K. Houk, Dissertation, Harvard (1968).

[92] R. C. Cookson, B. V. Drake, J. Hudec, and A. Morrison, *Chem. Commun.* 1966, 15; S. Itô, Y. Fujise, T. Okuda, and Y. Inoue, *Bull. chem. Soc. Japan* 39, 135 (1966).

[93] T. Nozoe, T. Mukai, K. Takase, and T. Takase, *Proc. Japan Acad.* 28, 477 (1952).

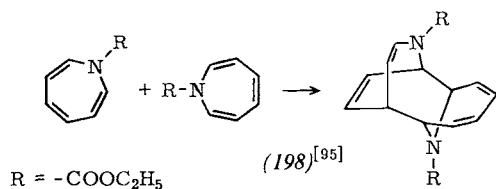
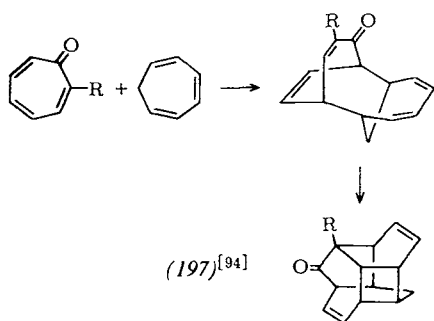
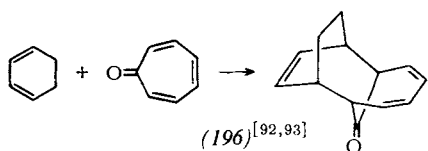
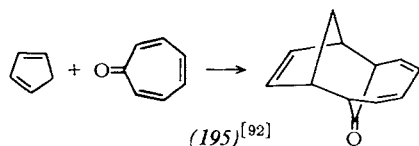
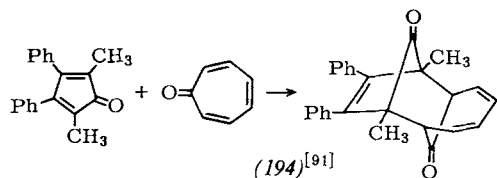
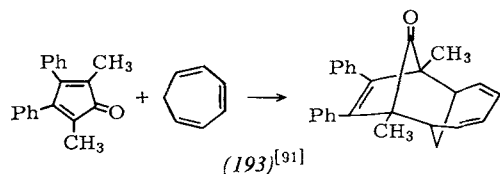
[94] S. Itô, Y. Fujise, and M. C. Woods, *Tetrahedron Letters* 1967, 1059.

[95] L. A. Paquette and J. H. Barrett, *J. Amer. chem. Soc.* 88, 2590 (1966).

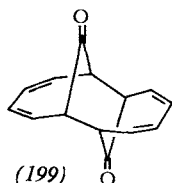
[96] H. E. Winberg, F. S. Fawcett, W. E. Mochel, and C. W. Theobald, *J. Amer. chem. Soc.* 82, 1428 (1960); D. J. Cram, C. S. Montgomery, and G. R. Knox, *ibid.* 88, 515 (1966); D. J. Cram, C. K. Dalton, and G. R. Knox, *ibid.* 85, 1088 (1963); D. T. Longone and F.-P. Boettcher, *ibid.* 85, 3436 (1963).

[97] T. Mukai, T. Tezuka, and Y. Akasaki, *J. Amer. chem. Soc.* 88, 5025 (1966).

[98] A. S. Kende and J. E. Lancaster, *J. Amer. chem. Soc.* 89, 5283 (1967).

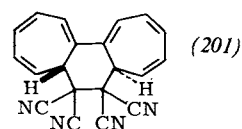
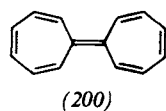


Heptafulvalene (200) combines with tetracyanoethylene to give the adduct (201), whose structure has been firmly established by X-ray crystallographic

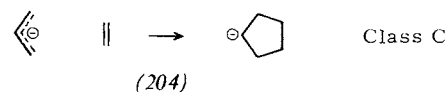
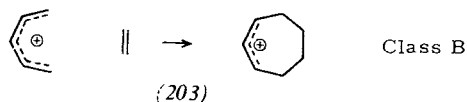
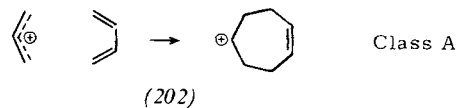


methods^[99]. The adduct is the expected product of the symmetry-allowed ground-state [$\pi 14_a + \pi 2_s$] process; it may be noted that the twisted shape of the heptafulvalene molecule sets the stage ideally for *antara* addition to the 14-electron system.

[99] W. von E. Doering, personal communication.



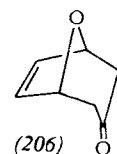
Cycloadditions involving ionic components are as yet not common. Ionic [4+2] cycloadditions may be realized in a number of different ways [(202)–(204)].



We may assign to class A the cycloaddition reactions of cyclopropanones (205). It is not unlikely that cyclopropanones are in equilibrium with an isomeric dipolar species. The latter can act as a 2 π -electron system, and,



predictably, combines with dienes in [$\pi 4_s + \pi 2_s$] processes – for example, with furans to give adducts of the type (206)^[100].



Most recently, the direct combination of the 2-methylallyl cation (207) with cyclopentadiene and with cyclohexadiene, to give the bicyclic cations (208), Z = -CH₂- or -CH₂-CH₂-, has been demonstrated^[101].



A remarkable cycloaddition of class B is that which occurs in the formation of the pipitzols (210) from perezone (209)^[102].

[100] R. C. Cookson, M. J. Nye, and G. Subrahmanyam, *J. chem. Soc. C*, 1967, 473; 1965, 2009; A. W. Fort, *J. Amer. chem. Soc.* 84, 2620, 2625, 4979 (1964); N. J. Turro and W. B. Hammond, *ibid.* 87, 3258 (1965); 88, 3672 (1966); W. B. Hammond and N. J. Turro, *ibid.* 88, 7880 (1966).

[101] H. M. R. Hoffmann, D. R. Joy, and A. K. Suter, *J. chem. Soc. B*, 1968, 57.

[102] F. Walls, J. Padilla, P. Joseph-Nathan, F. Giral, and J. Romo, *Tetrahedron Letters* 1965, 1577.