Figure 2. Correlation diagrams for the interconversion of cyclobutene and butadiene.
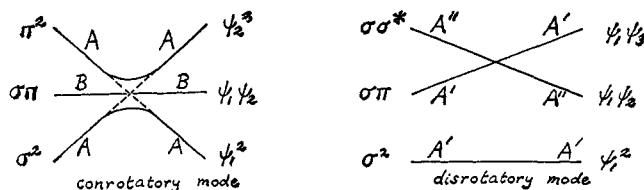

Figure 3. Interconversion of cyclopropyl cation and allyl cation.
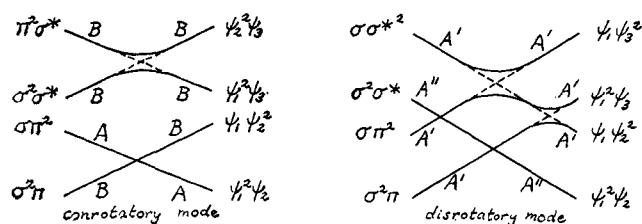

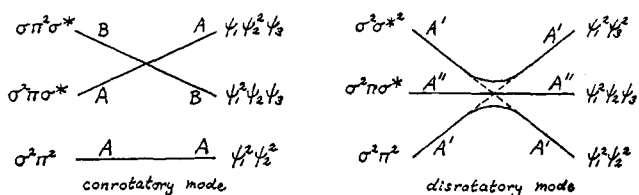Figure 4. Interconversion of cyclopropyl radical and allyl radical.

Figure 5. Interconversion of cyclopropyl anion and allyl anion.

Hoffmann. But for the radicals the situation is more complex. In both the conrotatory and disrotatory modes the ground state of each radical is correlated

Table II

		Cyclopropyl	Allyl
Conrotatory mode	A	σ	ψ_2
	B	π, σ^*	ψ_1, ψ_3
Disrotatory mode	A'	σ, π	ψ_1, ψ_3
	A''	σ^*	ψ_2

with an excited state of the other. If the excited states occur in the order shown (as one would suppose), the thermal reaction should be slightly less hindered in the conrotatory than in the disrotatory mode, but should show a much larger activation energy than the thermal transformation of the ions. One would therefore expect the thermal isomerization of the cyclopropyl radical to be much slower and probably much less stereospecific than for either the positive or the negative ion.

As to the photochemical transformations, the first excited state of either radical should also isomerize by the conrotatory mode, but in the second excited state, which lies very close above the first, disrotatory transformations are to be expected.

We have thought it worthwhile to supplement the discussion of Woodward and Hoffman in this way because orbital and state correlation diagrams enable one to follow a reaction along its entire course and draw qualitative conclusions without necessarily engaging in numerical computations.

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Received March 20, 1965

Selection Rules for Concerted Cycloaddition Reactions

Sir:

Recently we characterized orbital symmetry relationships as stereochemical determinants in electrocyclic reactions, which may be regarded as intramolecular cycloadditions, involving net interconversions of one π-bond and one σ-bond.[1] We now examine the general problem of concerted intermolecular cycloaddition reactions from a similar point of view.

Our procedure consists in the construction of correlation diagrams for the molecular orbitals involved in reaction, classifying the levels with respect to the symmetry elements of the transition state.[2] The method is illustrated first in the case of the addition of two ethylenes to form cyclobutane. The assumed geometry of approach places the two ethylene molecules in parallel planes directly above each other, as in Figure 1. The
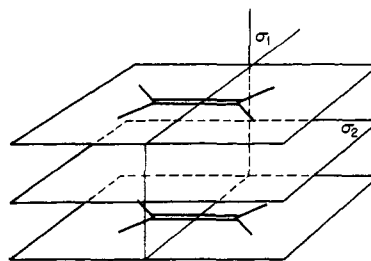

Figure 1.

four reactant π-levels and the four corresponding σ-levels in the product are shown in Figure 2, classified as symmetric (S) or antisymmetric (A) with respect to σ_1, a plane bisecting the ethylenes, and σ_2, a plane parallel to and midway between the planes of the approaching molecules. The form of the molecular orbitals, projected upon the plane passing through the four carbon atoms, is shown in Figure 3. The original

(1) R. B. Woodward and R. Hoffmann, J. Am. Chem. Soc., 87, 395 (1965).
(2) This method has been independently and elegantly used in a discussion of electrocyclic reactions by Professor H. C. Longuet-Higgins (Cambridge), who very kindly communicated his results to us privately prior to publication.
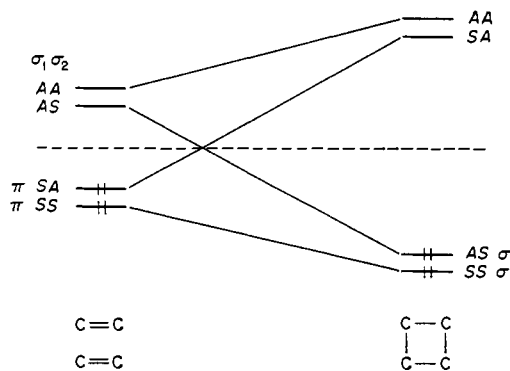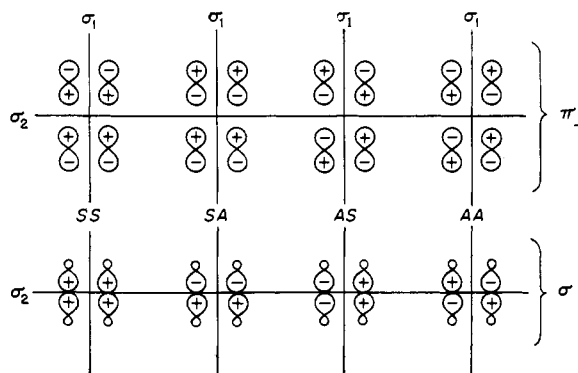
Figure 2.

Figure 3.

Figure 4.

Figure 5.

Figure 6.

ethylene π-bonding orbitals combine into the SS- and SA-orbitals of the interacting system, but the final σ-bonding orbitals are SS and AS. Note that πSS and πAS are bonding in the region of reaction and so decrease in energy along the reaction coordinate, while πSA and πAA are antibonding and so increase in energy. A level crossing results and is confirmed by extended Hückel calculations.

We consider next the combination of ethylene and butadiene. The transition state is formulated with diene and dienophile in parallel planes, and a perpendicular plane of symmetry σ_1, bisecting the molecules, as in Figure 4. Again a correlation diagram is drawn (Figure 5), relating the six reactant π-levels (four butadiene plus two ethylene) and the two resultant π- and four σ-orbitals. The three S-orbitals interact so that the lowest one (originally the diene most bonding π) decreases in energy, the highest S-level (originally the first unoccupied diene level) increases, while the middle S component (initially the ethylene π-level) remains at nearly constant energy; a similar pattern of interaction obtains for the A-orbitals. An extended Hückel calculation confirms the level scheme and shows some charge transfer from diene to olefin in the transition state, resulting primarily from mixing of the antibonding ethylene A level into the highest occupied diene A.

When the diagrams for the 1,2 and 1,4 additions are compared, it is clear that the bonding–antibonding level correlation in 1,2 addition makes this a highly unfavorable ground-state process, while no comparable factor mitigates against the 1,4 addition. On the other hand, if in each case one electron is excited to the next higher level, the energy along
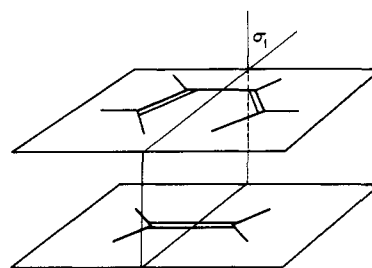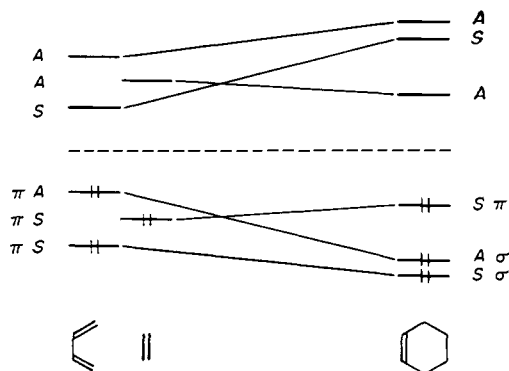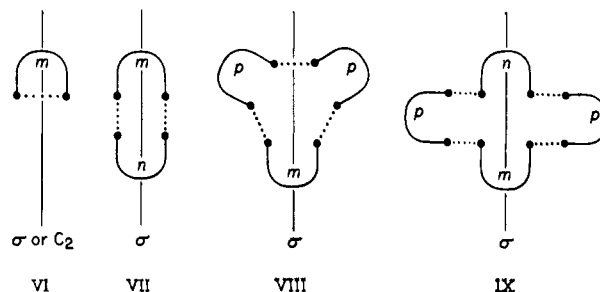
the reaction path is decreased for the 1,2 addition and increased for the 1,4 process. If now we make the reasonable postulate that, in general, correlation diagrams resembling that of Figure 5, i.e., having no correlations of bonding with antibonding orbitals, are characteristic of permitted thermal reactions, while schemes similar to that of Figure 2, with bonding–antibonding correlations, are typical of photochemical processes, one can derive the following selection rules for the concerted cycloaddition reactions illustrated here (VI-IX) (m, n, p are numbers of π-electrons, q is an integer 0, 1, 2, 3 ....).

(1) Electrocyclic reactions (VI) (one π-bond $\rightarrow$ one σ-bond) will be thermally disrotatory and photochemically conrotatory for $m = 4q + 2$, thermally conrotatory and photochemically disrotatory for $m = 4q$. (2) The $2\pi \rightarrow 2\sigma$ process (VII) will be allowed thermally for $m + n = 4q + 2$, photochemically for $m + n = 4q$. (3) The $3\pi \rightarrow 3\sigma$ reaction, with a plane of symmetry bisecting m (VIII), will be allowed thermally for $m = 4q + 2$ (any p), photochemically for $m = 4q$ (any p). (4) The $4\pi \rightarrow 4\sigma$ process (IX) will be allowed thermally for $m + n = 4q + 2$ (any p), photochemically for $m + n = 4q$ (any p).

The proofs consist of enumeration of, say, bonding S-levels in reactants and products. If the number of bonding S-levels does not change, there will be no bonding → antibonding correlations, and the process is thermally allowed. If the number of bonding S-levels is one less or one greater in the product, a crossing must occur. As an example, consider the $2\pi \rightarrow 2\sigma$ case. In one component, containing, for example, m π-orbitals in the reactant, there will be $m/4$ bonding π-orbitals of S symmetry if $m/2$ is even, $(m + 2)/4$ if $m/2$ is odd. In the same component of the product, now containing $(m - 2)$ π-orbitals, there will be $m/4$ bonding S-levels if $m/2$ is even, $(m - 2)/4$ if $m/2$ is odd. The product σ-levels will yield one bonding level of S symmetry; thus, the total number of bonding S-levels from the reactant π's must exceed by one that from the product π's for a thermally allowed reaction. There are three cases: (1) $m = 4q_1$, $n = 4q_2$; then there will be $(q_1 + q_2)$ π-bonding S-levels before, $(q_1 + q_2)$ after. (2) $m = 4q_1 + 2$, $n = 4q_2$; this implies $(q_1 + q_2 + 1)$ before, $(q_1 + q_2)$ after. (3) $m = 4q_1 + 2$, $n = 4q_2 + 2$; this implies $(q_1 + q_2 + 2)$ before, $(q_1 + q_2)$ after. Case 2 satisfies the condition for the thermal process, and it is therefore required that $m + n = 4q_1 + 4q_2 + 2 = 4q + 2$; cases 1 and 3 will lead to bonding → antibonding correlations.

Certain special points concerning our selection rules deserve mention: (i) they apply to all concerted cycloaddition reactions, even though there may be considerable asymmetry in the rate at which the various different newly forming σ-bonds are established.[3] (ii) They need not apply to multistep cycloaddition reactions which proceed through discrete diradical or dipolar *intermediates*, containing a single newly formed σ-bond.

We may now tabulate the smaller ($\Sigma\pi \leqslant 10$) allowed concerted cycloaddition reactions (Table I). In point of

Table I

Type	Thermal				Photochemical			
$2\pi \rightarrow 2\sigma$ (VII)	m	n			m	n		
	4	2			2	2		
	6	4			4	4		
	8	2			6	2		
$3\pi \rightarrow 3\sigma$ (VIII)	m	p	p		m	p	p	
	2	2	2		4	2	2	
	2	4	4					
	6	2	2					
$4\pi \rightarrow 4\sigma$ (IX)	m	n	p	p	m	n	p	p
	4	2	2	2	2	2	2	2

fact, the agreement with recorded experience is outstanding. Examples are well known which very probably follow the allowed thermal 4 + 2 (Diels–Alder reaction) and 2 + 2 + 2[4] processes, and the allowed photochemical 2 + 2[5] and 4 + 4[6] cases, though the

(3) As in the mechanism earlier proposed for the Diels–Alder reaction by one of us [R. B. Woodward and T. J. Katz, *Tetrahedron*, 5, 70 (1959).

(4) Norbornadiene + olefins, A. T. Blomquist and Y. C. Meinwald, *J. Am. Chem. Soc.*, 81, 667 (1959); 1,3,5,7-tetramethylenecyclooctane + tetracyanoethylene, J. K. Williams and R. E. Benson, *ibid.*, 84, 1257 (1962).

(5) Numerous cases cited in the review by R. Huisgen, R. Grashey, and J. Sauer in "The Chemistry of the Alkenes," S. Patai, Ed., John Wiley and Sons, Inc., New York, N. Y., 1964, p. 739.

relevant concerted reactions may well be substantially electronically unsymmetrical. But it must be emphasized that the nature of our relations as *selection rules* makes the allowed cases *permissive*, but not *obligatory*; consequently, the rules do not *per se* exclude multistep alternative mechanisms involving discrete intermediates. By the same token, it must be concluded that those cycloadditions which do occur in cases prohibited by our selection rules for concerted reactions must proceed through multistep mechanisms (*e.g.*, formation of cyclobutane derivatives by dimerization of allenes and ketenes, and additions of perhalo- and percyanoethylenes to olefins, as well as dimerizations of *p*-xylylenes and the rarely observed photochemical Diels–Alder reaction), a conclusion in good accord with emerging experience.[7]

In assessing the predictive power of our selection rules in discerning possible new reactions, the following special points should be kept in mind: (i) (*restrictive*) the activation energies for thermal reactions should increase with the total number of π-electrons, as the total of bond elongations and contractions increases in the transition state; (ii) (*restrictive*) unless special geometrical constraints are present, entropy factors can place severe barriers in the way of realization of more complicated cases; (iii) (*extensive*) the relationships apply to ionic components as well as to neutral molecules, *e.g.*, allyl cation + cyclopentadiene → bicyclo[1.2.3]octenyl cation is permitted, while allyl cation + ethylene → cyclopentyl cation is prohibited.

The theoretical method used here has very wide applicability. We have already extended it to include the Cope and related rearrangements, and in studies of valence tautomers of $(CH)_n$; these results will form the subject of future communications.

(6) α-Pyridones: L. A. Paquette and G. Slomp, *J. Am. Chem. Soc.*, 85, 765 (1963); α-pyrones: P de Mayo and R. W. Yip, *Proc. Chem. Soc.*, 84 (1964); anthracenes: D. E. Applequist and R. Searle, *J. Am. Chem. Soc.*, 86, 1389 (1964); naphthalenes: J. S. Bradshaw and G. S. Hammond, *ibid.*, 85, 3953 (1963).

(7) *Cf.* P. D. Bartlett, L. K. Montgomery, and B. Seidel, *ibid.*, 86, 616 (1964); L. K. Montgomery, K. Schueller, and P. D. Bartlett, *ibid.*, 86, 622 (1964); P. D. Bartlett and L. K. Montgomery, *ibid.*, 86, 628 (1964), and references there cited.

(8) Junior Fellow, Society of Fellows, Harvard University.

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Salt-Like Behavior of the *t*-Butyl Chloride Solvolysis Transition State[1,2]

Sir:

One of the most intriguing results in physical organic chemistry is the plot of Winstein and Fainberg's[3] activation parameters for the solvolysis of *t*-butyl chloride in a series of aqueous ethanol solutions, a portion of which is reproduced in Figure 1. Although enthalpy-entropy plots are linear for many properties of many

(3) S. Winstein and A. H. Fainberg, *J. Am. Chem. Soc.*, 79, 5937 (1957).