

Correlation Diagrams-II

C734b 2008

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Electrocyclic Reactions

Example: Butadiene-cyclobutene conversion

Ring closure of polyolefins and the reverse ring opening process are referred to as *electrocyclic reactions*.

Orbitals used for π -bonding in a particular olefin are used for σ -bonding in the cyclic compound

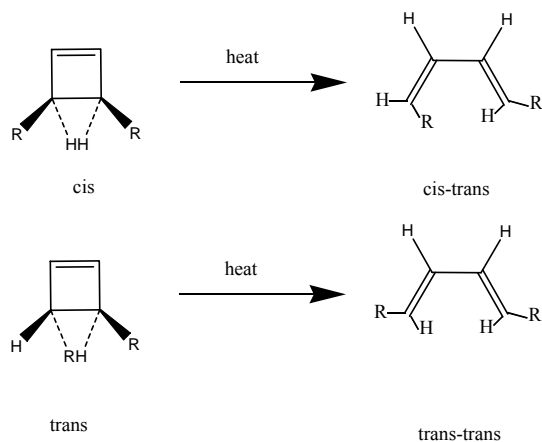
Reactions are stereospecific.

Woodward and Hoffman showed that the products depend on the number of π -electrons in the polyolefin, and the products differ for thermal and photochemical reactions.

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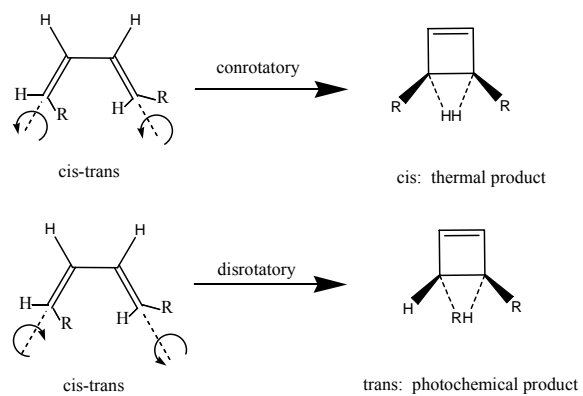
Example: heating *cis*-3,4-dimethylcyclobutene gives *cis-trans*-2,4-hexadiene, while heating *trans*-3,4-dimethylcyclobutene gives *trans-trans*-2,4-hexadiene.



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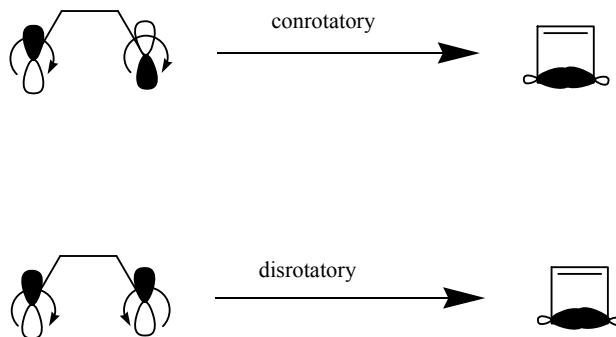
The photochemically-induced cyclization reaction yield the opposite isomers of dimethylcyclobutene



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Definitions



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Woodward-Hoffman Rules

Orbital symmetry must be preserved in concerted reaction; this requires that one or more symmetry elements persist from reaction initiation to completion; that is, during the bond-breaking or bond-formation.

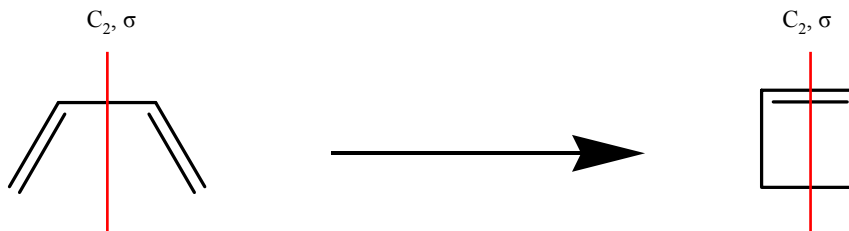
The molecular orbitals (or electronic states) must belong to the same symmetry species of the point group of the reacting system during the entire course of the reaction.

If the filled low-energy orbitals of the reactant(s) correlate with high-energy orbitals of the product(s), there will be a high activation energy, and the reaction will be *symmetry-forbidden*.

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Example: the reaction of butadiene to make cyclobutene.



Symmetry elements which persist are a C_2 axis if the orbital motion is conrotatory or a reflection plane σ if the orbital motion is disrotatory

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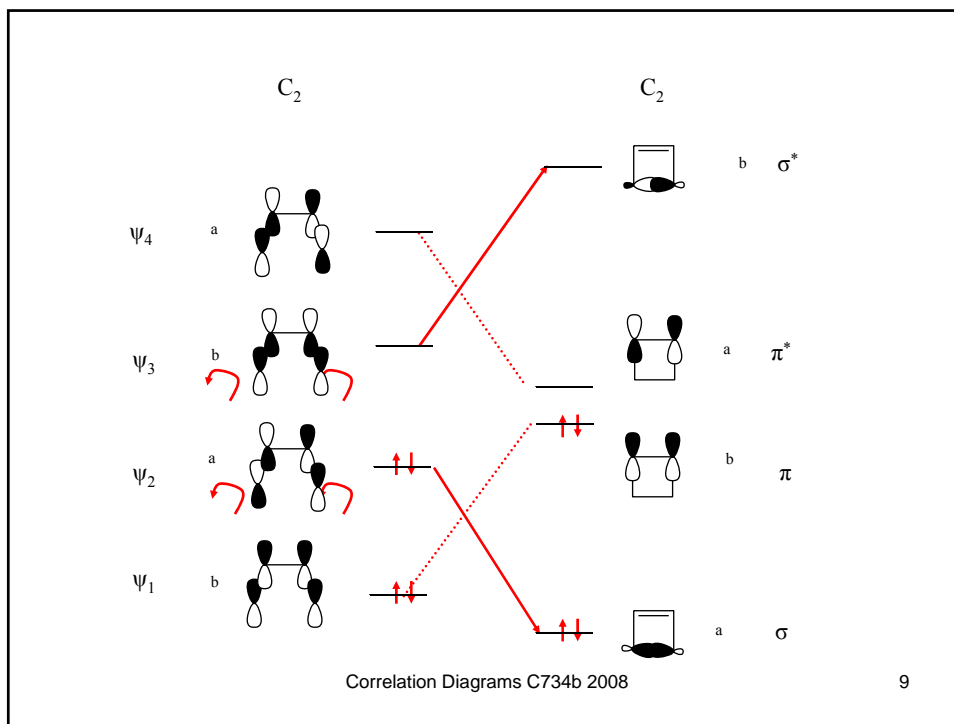
Conrotatory motion

During this motion, the C_2 symmetry element is preserved.

Consider the MOs of reactants and the products, and label them with respect to the C_2 operation; that is, if the MO is symmetric with respect to C_2 then label the MO a, and if it is antisymmetric with respect to C_2 , label it b.

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Note:

The bonding ψ_2 orbital of butadiene (HOMO) correlates with bonding σ -orbital of cyclobutene.

The anti-bonding ψ_3 orbital of butadiene correlates with anti-bonding σ^* -orbital of cyclobutene.

The orbital sign pattern for the bonding ψ_1 matches that of bonding π -orbital of cyclobutene as does that the anti-bonding ψ_4 orbital and the anti-bonding π^* -orbital of cyclobutene.

Conclude: that the conrotatory process **is symmetry-allowed** because the bonding orbitals of the reactant correlate with the bonding orbitals of the product with the same symmetry.

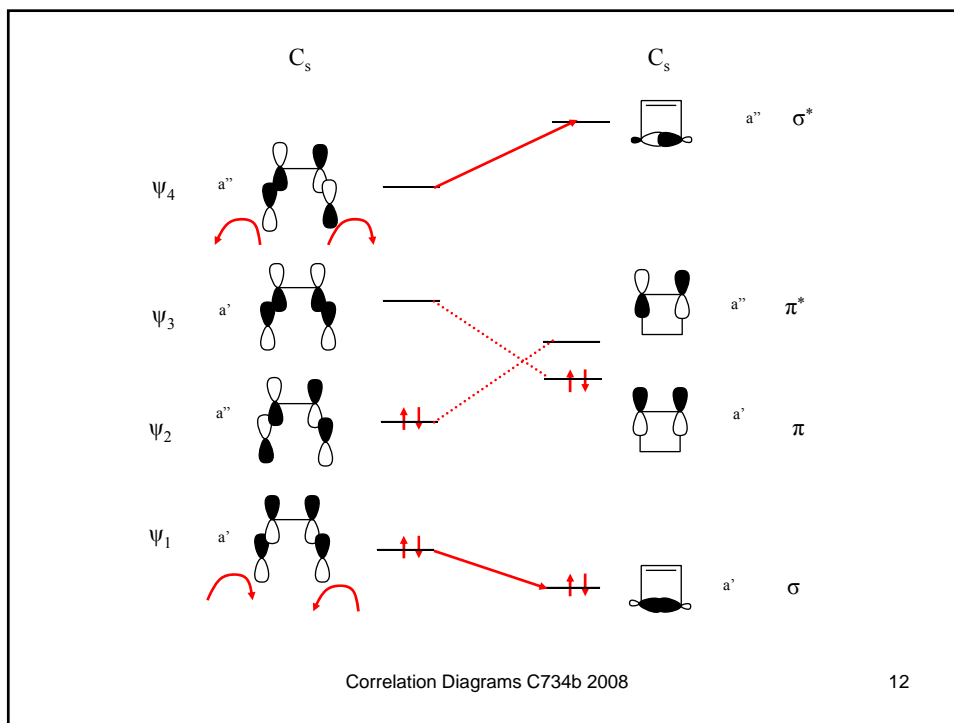
Disrotatory motion

During this motion, the σ symmetry element is preserved.

Consider the MOs of reactants and the products, and label them with respect to the σ operation; that is, if the MO is symmetric with respect to σ then label the MO a' , and if it is antisymmetric with respect to σ , label it a'' .

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Note:

The bonding ψ_2 orbital of butadiene correlates with ant-bonding π -orbital of cyclobutene.

The anti-bonding ψ_3 orbital of butadiene correlates with bonding π -orbital of cyclobutene.

Conclude: that the disrotatory process **is symmetry-forbidden** because the bonding orbitals of the reactant correlate with the bonding orbitals with the same symmetry of the product.

Other notes:

The HOMO remains a bonding MO only for the symmetry-allowed reaction for the conrotatory reaction.

This is not surprising since the HOMO is intimately allowed in the reaction and will restrict the course of the reaction.

Therefore: promote the electron from ψ_2 to ψ_3 photochemically which now becomes the HOMO.

Since ψ_3 HOMO of butadiene correlates with the π -orbital of cyclobutene the reaction now becomes symmetry-allowed for a conrotatory process, but symmetry-forbidden for a disrotatory process. This is because in the latter case ψ_3 correlates with the anti-bonding σ^* -orbital of cyclobutene.

A feeling for Diels-Alder Reactions

Concerted cycloaddition reaction involving the addition of a substituted alkene and a conjugated diene.

Simplest example: the addition of an olefin to 1,3-butadiene.

One reactant has 4π electrons and one has 2π electrons.
This is considered therefore a $[4+2]$ cycloaddition.

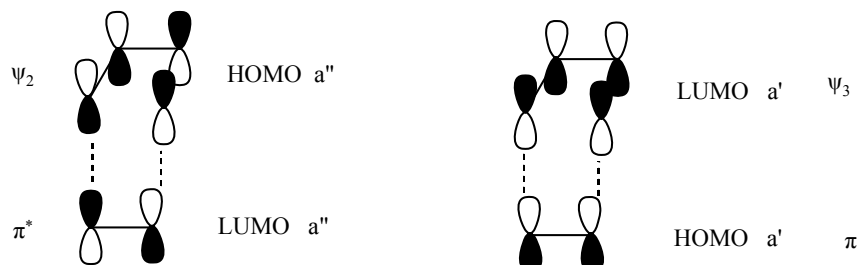
For addition to occur the π -orbitals of the terminal carbons of 1,3-butadiene must overlap that of the olefins symmetrically so that two σ -bonds can be formed simultaneously as the π -bonds are broken.

Once again a symmetry plane persists throughout the reaction which means that the orbitals are labelled a' if they are symmetric with respect to reflection and a'' if they are antisymmetric.

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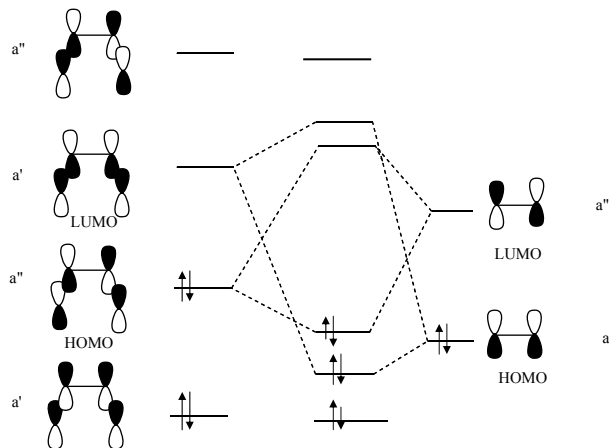
Two combinations are symmetry allowed:



Combinations leads to one MO lower in energy than the HOMO and one MO higher in energy than the LUMO involved. Knowing this can help construct an orbital correlation diagram

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Reaction will proceed thermally.

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Similar argument can be used to show that the [2+2] cycloaddition of two ethylenes to make cyclobutane is not allowed but can be made to go photochemically.

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