

**18 Feb 1999**

## *Concerted Reactions: Electrocyclic Processes*

### **Some Definitions...**

- **- bond-making and bond-breaking occur simultaneously (as compared to in a step-wise fashion).**
- **- bond-breaking is exactly compensated for by bond-making.**
- **- bond-breaking might lead bond-making.**

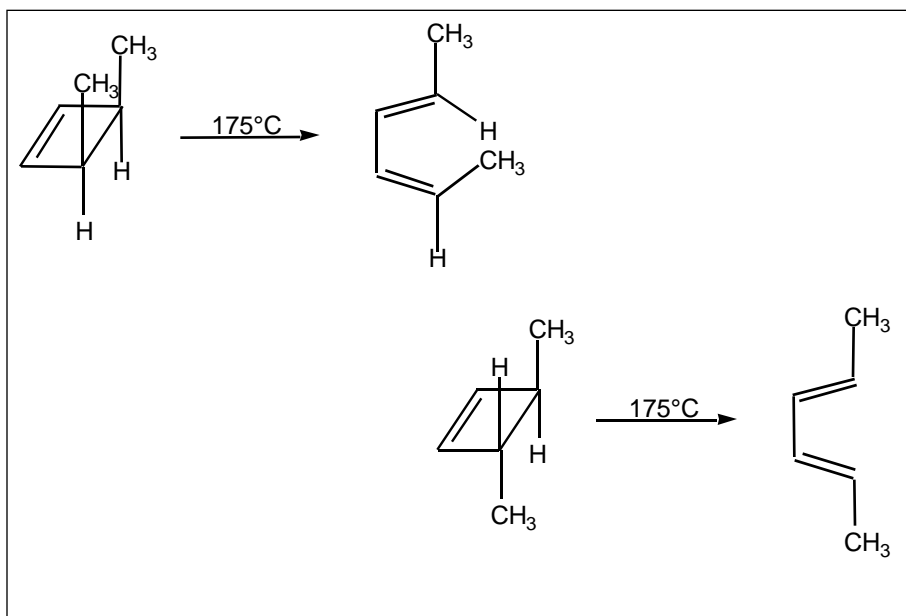
## Some Definitions...

- **Electrocyclic reaction** - as defined by Woodward and Hoffmann., "... in which concerted reorganization of bonding occurs through a cyclic array of continuously bonded atoms."
- **Electrocyclic reactions**
- **Sigmatropic rearrangements**
- **Group Transfer Reactions**
- **Ene Reaction**
- **Cycloaddition Reactions**
- **Cheletropic Reactions**

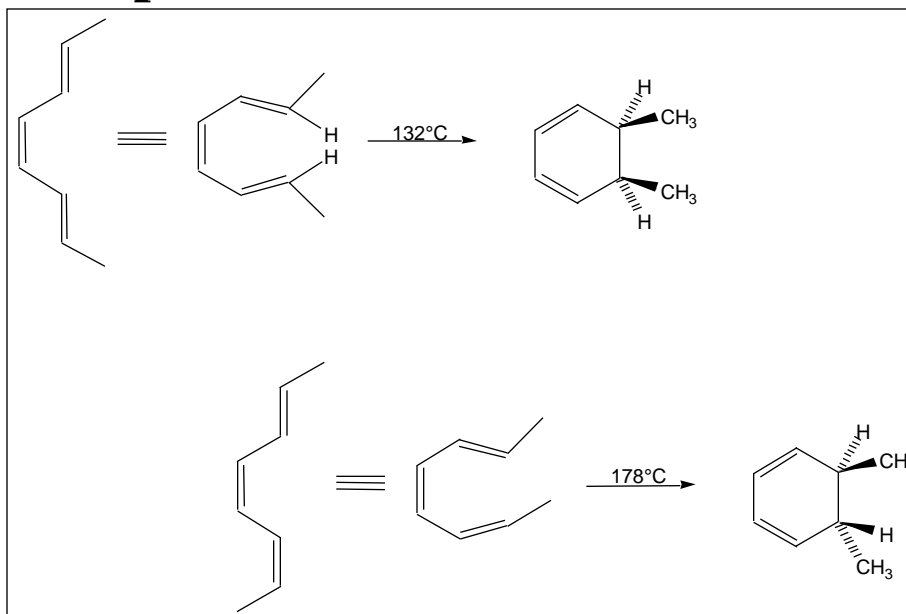
## Some Definitions...

- **Diels-Alder Reaction** - formation of a single bond between the ends of a linear system of electrons (& vice versa).
- **Electrocyclic Reaction** - ring opening/closing occurring via interconversion of  $\sigma$  - and  $\pi$  -bonds.
- **Diels-Alder Reaction** - formation of a single bond between the termini of an acyclic conjugated pi system containing  $\pi$  -electrons or the reversal of such a reaction.

## Example-thermal ring-opening of cyclobutenes.



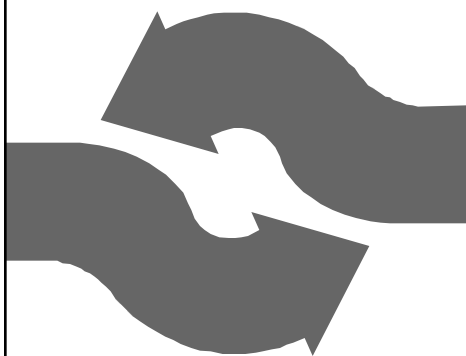
## Example-thermal ring-opening of cyclohexadienes.



## Wanted....

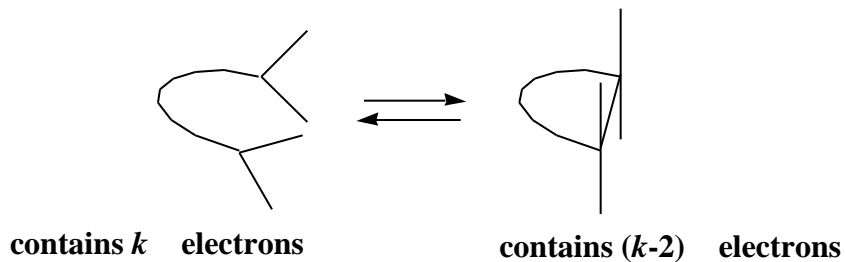
- **Mechanistic explanation req'd to explain...**
- **... high stereospecificity.**
- **... E,Z  $\rightarrow$  cis in 4-memb ring system**

## Reminder...



**Principle of Microscopic Reversibility** - lowest energy pathway for conversion of A  $\rightarrow$  B is also lowest energy pathway for B  $\rightarrow$  A (e.g., all rxns are reversible; the transition state for the forward and reverse reaction is identical).

## General Electrocyclic Reactions

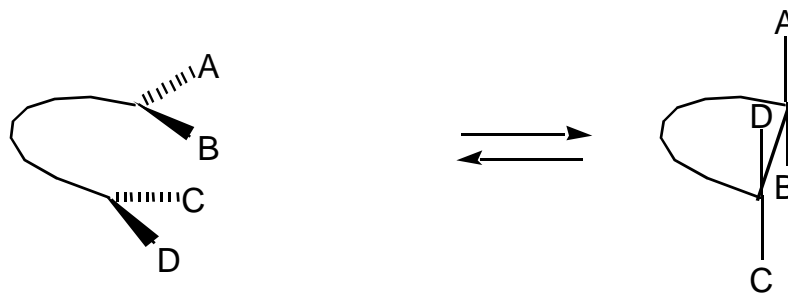


Open chain system - has fixed geometrical isomerism imposed on it by the alkenes.

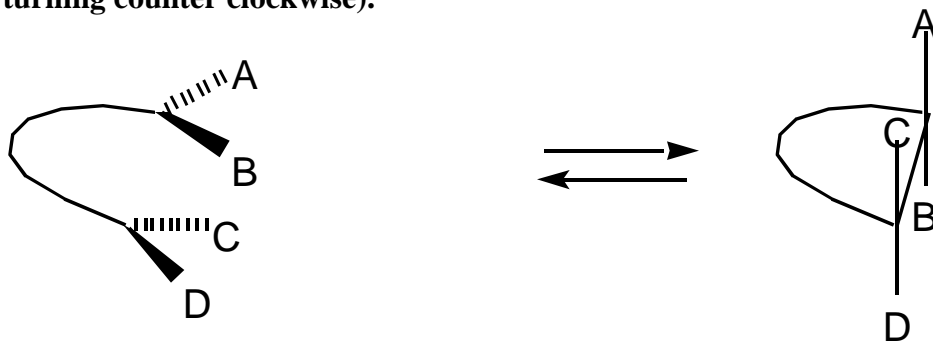
Cyclic array - rigid tetrahedral structure.

Possible pathways for electrocyclic reactions...

– the substituents on the two termini rotate in different directions; one turning clockwise and the other turning counterclockwise

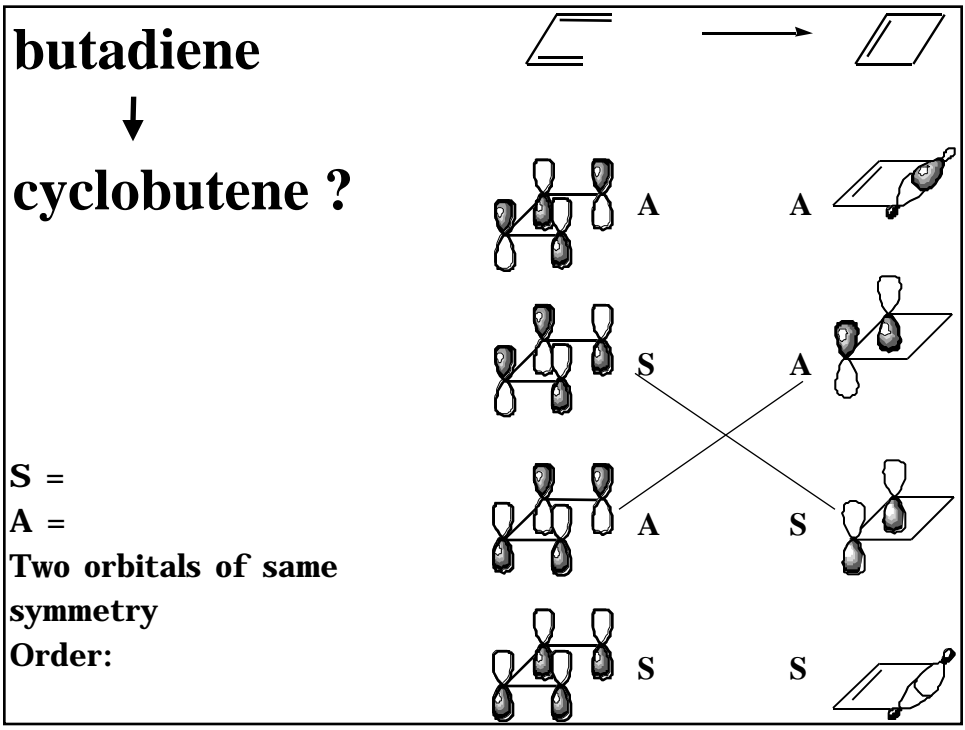
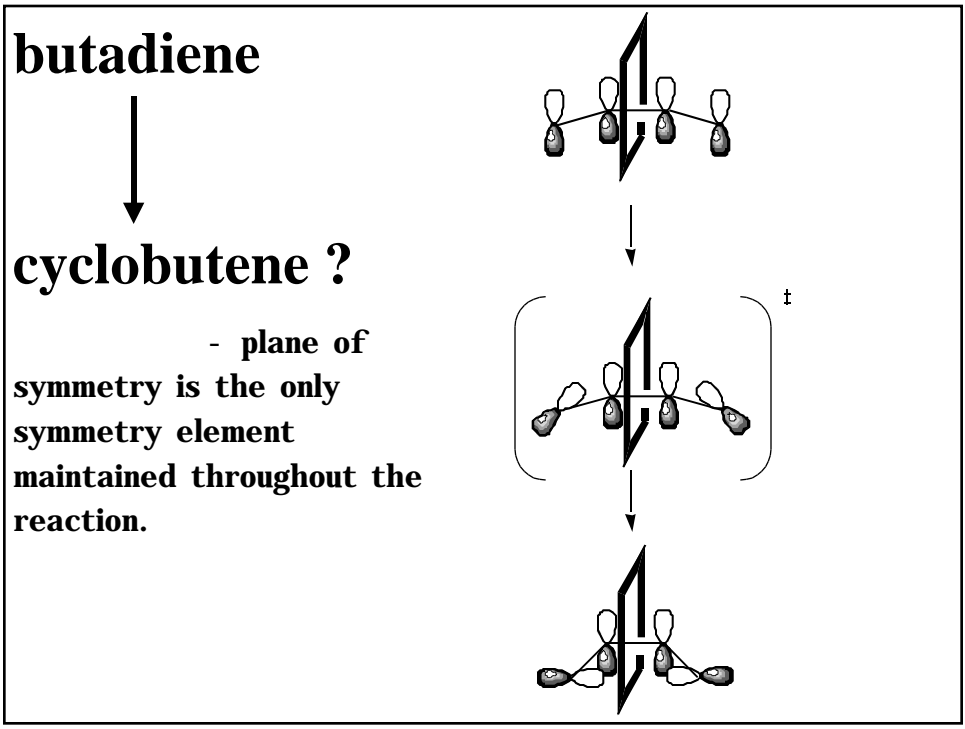


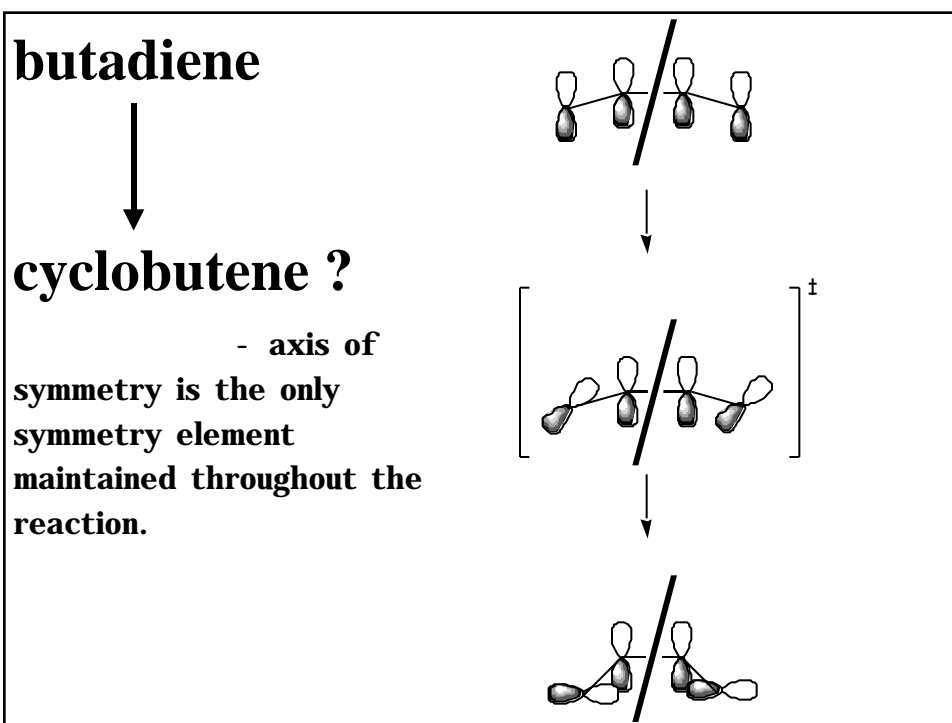
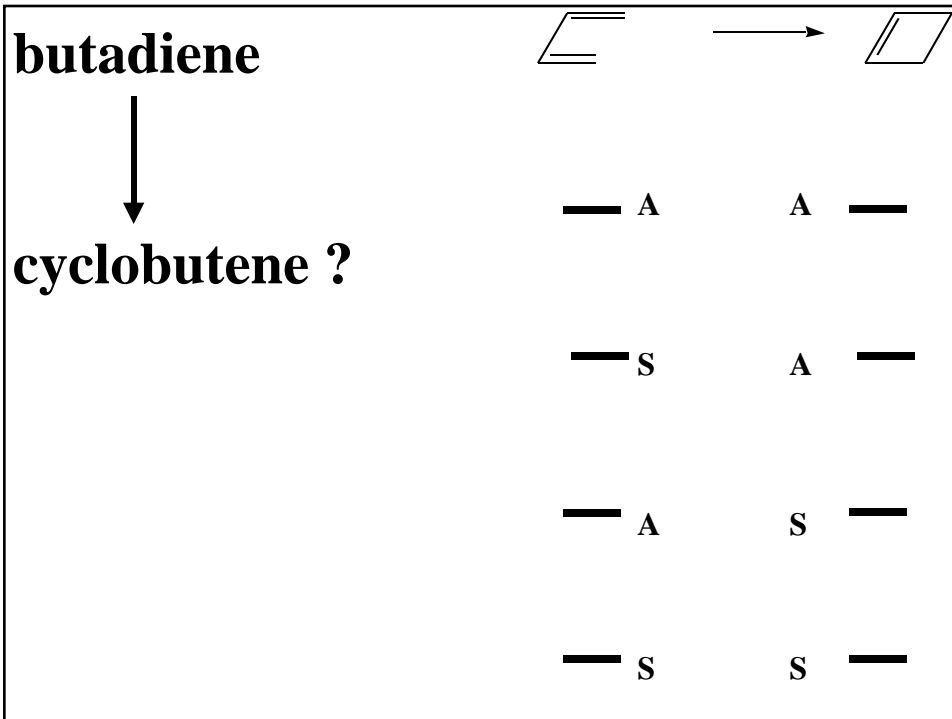
– the substituents on the two termini rotate in the same direction; one turning clockwise and the other turning clockwise (or both turning counter clockwise).

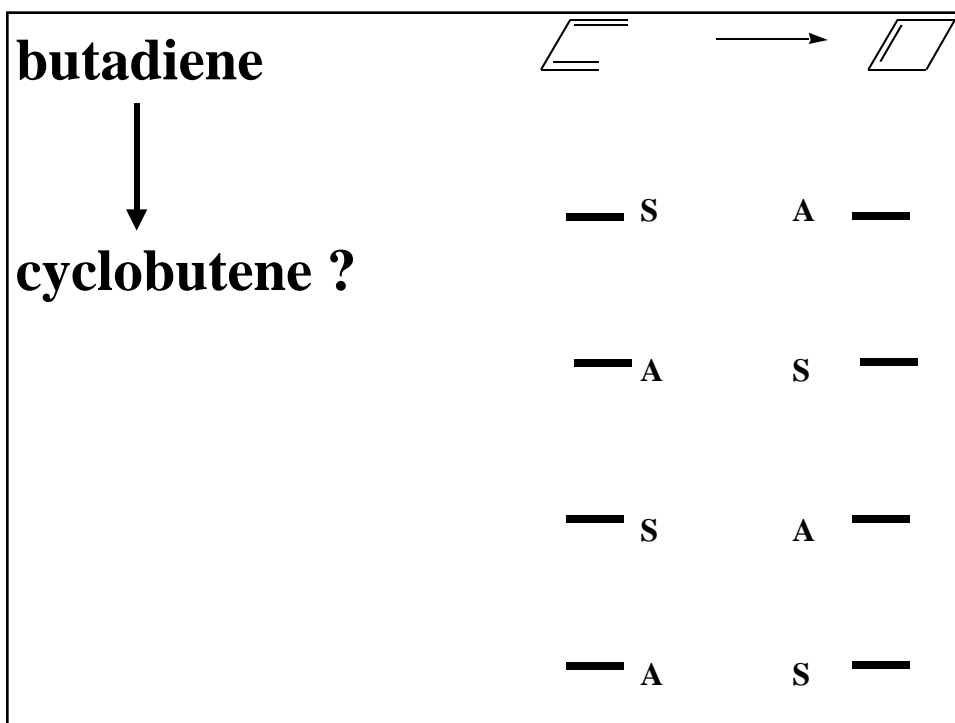
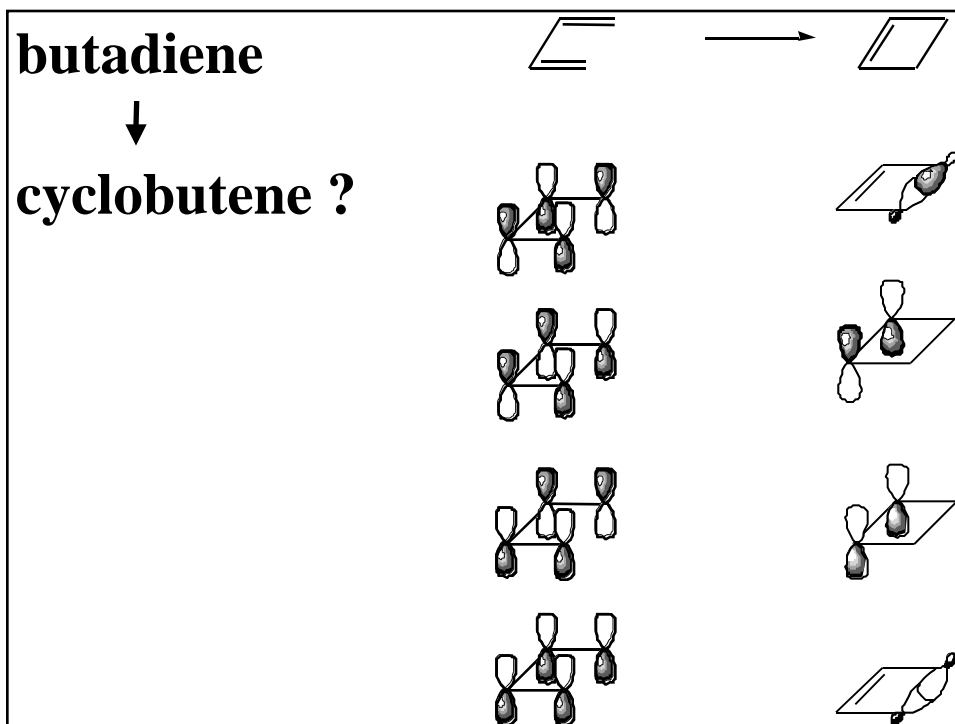


## The Conservation of Orbital Symmetry

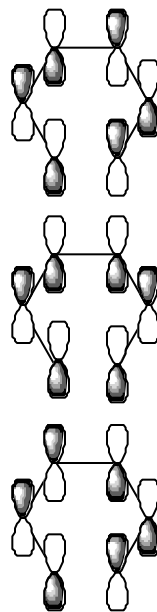
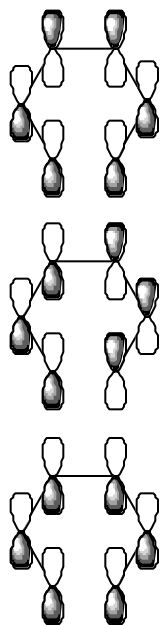
- Woodward & Hoffman, 1971
  - A reaction is allowed only when all the reactant bonding electrons are transferred without a symmetry-imposed barrier, into bonding orbitals of the products.



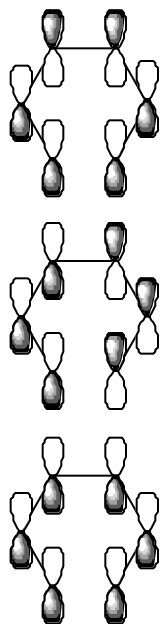


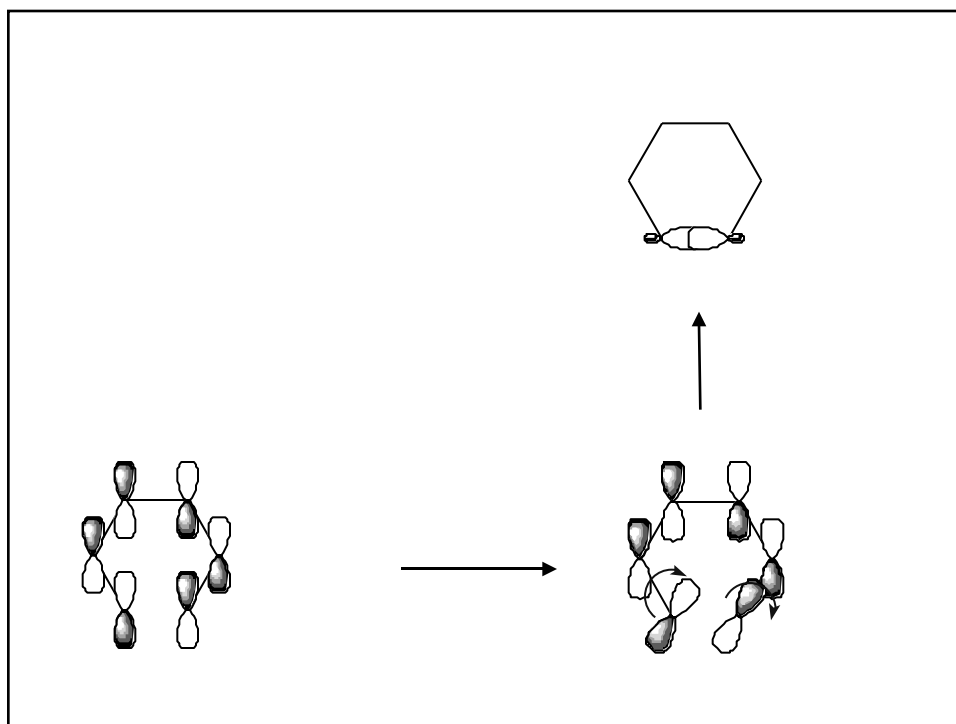


**hexatriene**



**hexatriene**

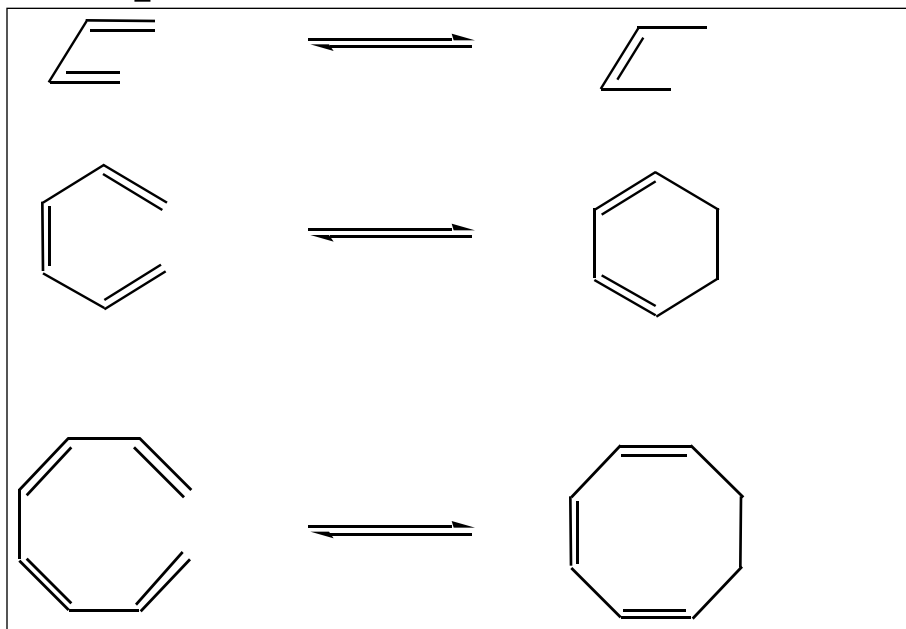




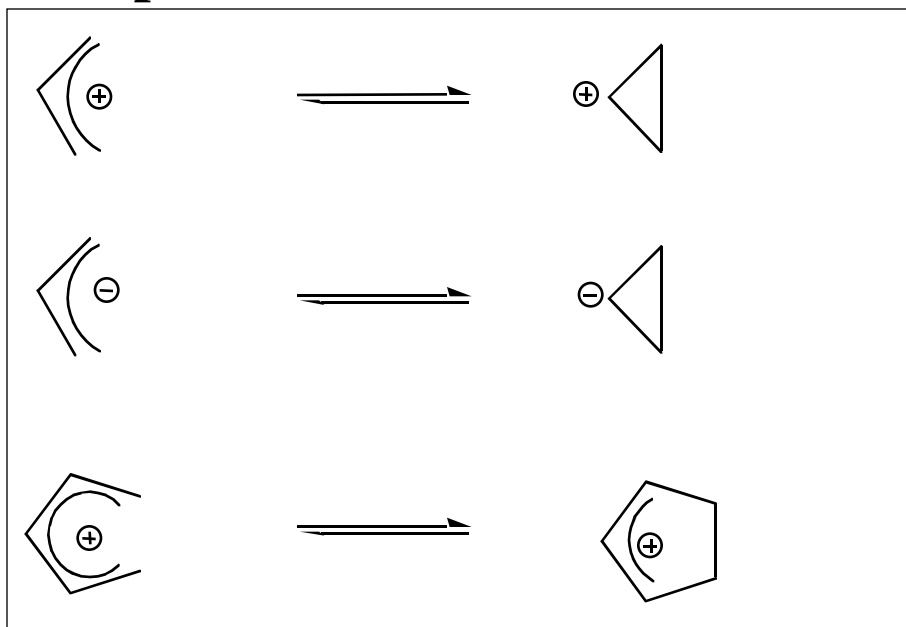
## **Selection Rule for Electrocyclic Transformation**

**If there are  $4n + 2$  electrons in a system of adjacent, parallel p orbitals undergoing an electrocyclic closure, then the reaction will be allowed thermally in the disrotatory fashion and allowed photochemically in the conrotatory fashion. If there are  $4n$  electrons, it will be allowed thermally conrotatory and photochemically disrotatory.**

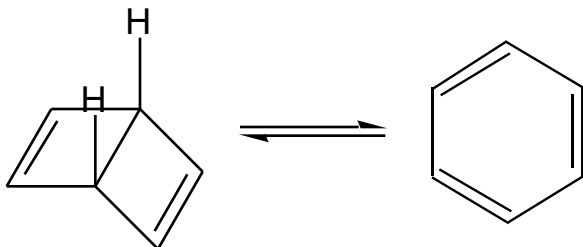
**Example... (Td = 6)**



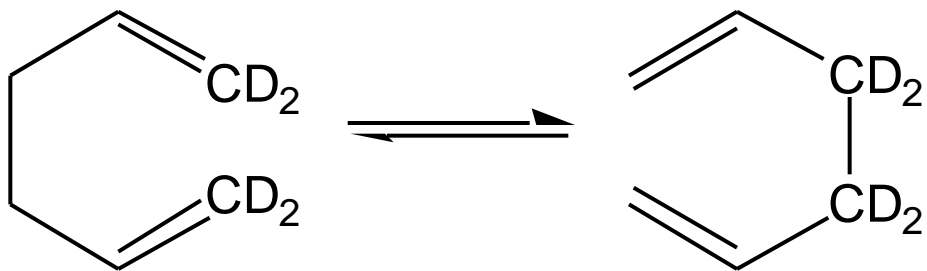
**Example... (Td = 6)**

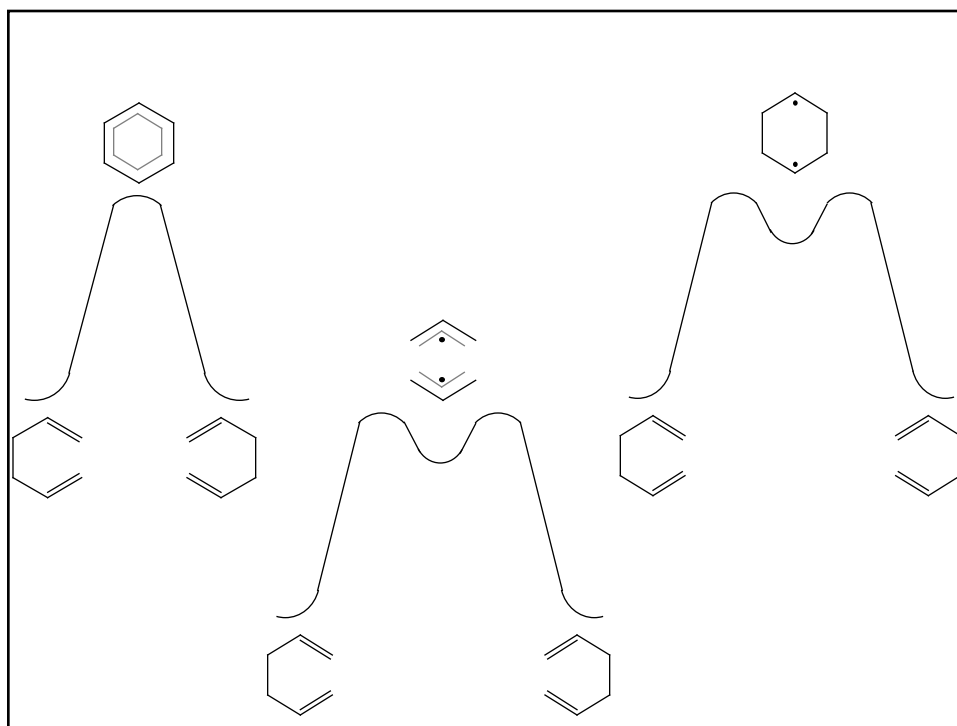


## Dewar Benzene

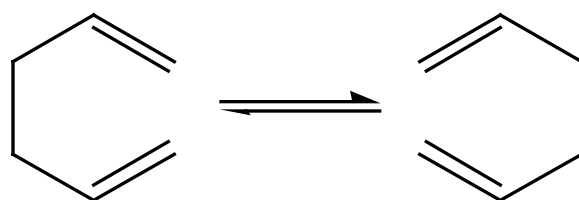


## Cope Rearrangement





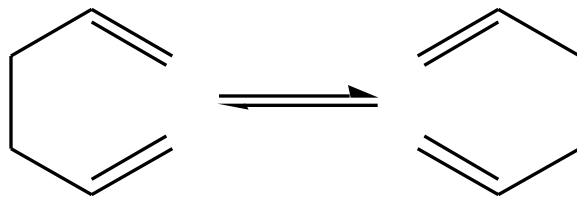
## Cope Rearrangement



Expt'l:

$H_f(\text{C}) =$	$\text{kcal/mol}$
$H^\ddagger =$	$\text{kcal/mol}$
$H_f(\text{TS}) = \text{kcal/mol}$	

## Cope Rearrangement



$$\text{BDE}(\text{H}_2\text{C}=\text{CC}-\text{CH}_2-\text{H}) = 86.6 \text{ kcal/mol}$$

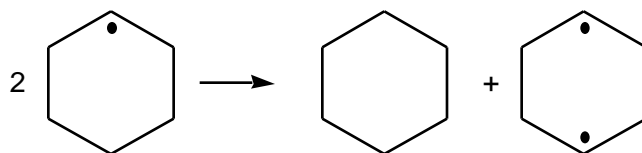
$$\text{H}_f(\text{H}_2\text{C}=\text{CH}-\text{CH}_3) = 4.88 \text{ kcal/mol}$$

$$\text{H}_f(\text{H}\bullet) = 52.1 \text{ kcal/mol}$$

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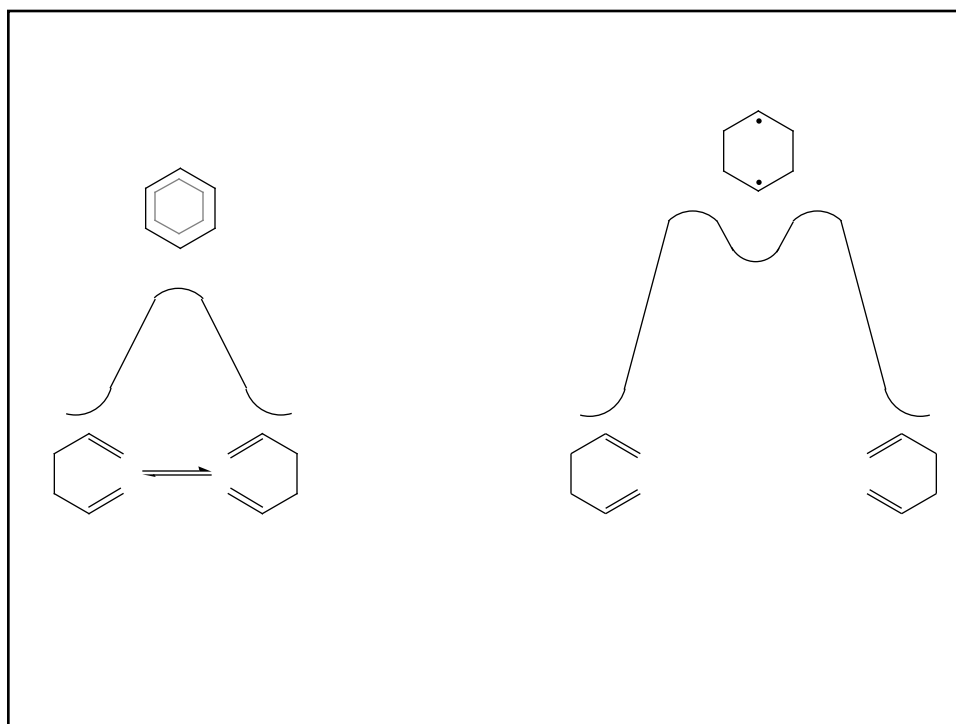

$$\text{H}_f(\text{H}_2\text{C}=\text{CH}-\text{CH}_2\bullet) = \quad \text{kcal/mol}$$

## Cope Rearrangement



$$\text{H}_{\text{rxn}} = 0 = \text{H}_f(\text{cyclohexane}) + \text{H}_f(\text{diyl}) - 2 \text{H}_f(\text{cyclohexyl radical})$$

$$\text{H}_f(\text{diyl}) = 2 \text{H}_f(\text{cyclohexyl radical}) - \text{H}_f(\text{cyclohexane})$$



## End Lecture

Electrocyclic Reactions

Energy of Concert