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# Chapter 1

# Pericyclic Reactions

## 1.1. Introduction:

**Definition:**

Pericyclic reactions are concerted processes that occur by way of a cyclic transition state in which more than one bond is formed or broken within the cycle.

The classic example of such a process is the Diels–Alder cycloaddition reaction, one of the most common and useful synthetic reactions in organic chemistry.

Cycloaddition reactions, sigma tropic rearrangements and electrocyclic reactions all fall into the category of pericyclic processes.

1. Concerted reaction that proceed via a cyclic transition state
2. No distinct intermediates in the reaction
3. Bond forming and bond breaking steps are simultaneous but not necessarily Synchronous

**Classification:**

- i. Electrocyclic ring closing and ring opening reaction
- ii. Cycloaddition and Cyclo-reversion reaction
- iii. Sigmatropic Rearrangements
- iv. Chelotropic Reaction
- v. Group transfer Reaction

**Sub Classification:**

Based on the number of π electrons involved in each component

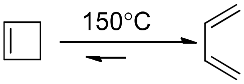
- i. The numbers are written within a square bracket e.g. [2π + 2π], [2π + 4π] etc
- ii. Electrocyclic ring closing and ring opening reaction (6pi), (4pi),
- iii. Cycloaddition and Cyclo-reversion reaction (6pi), (4pi),
- iv. Sigmatropic Rearrangements (3,3), (1,5), (1,3), (1,7),(2,3),Chelotropic Reaction
- v. Group transfer Reaction (related to sigmatropic)

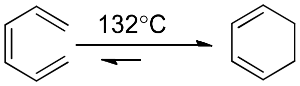
## 1.2. Electrocyclic Reactions:

Electrocyclizations, a class of pericyclic reactions, are characterized by the formation of a ring from an open-chain conjugated system, with a α-bond forming across the ends of a conjugated system (or vice-versa). Electrocyclization reactions can occur thermally or photochemically, via two possible modes known as conrotatory and disrotatory. The simplest examples of thermal electrocyclization are illustrated in below figure.

**OR**

An electrocyclic reaction is defined as the thermal or photochemical conversion of an acyclic conjugated system into a ring system by formation of a σ bond between the ends of the conjugated system in a concerted process, or the reverse of this reaction. These reactions are reversible in nature.





Woodward–Hoffmann rules for electrocyclic reactions are summarized in below Table:

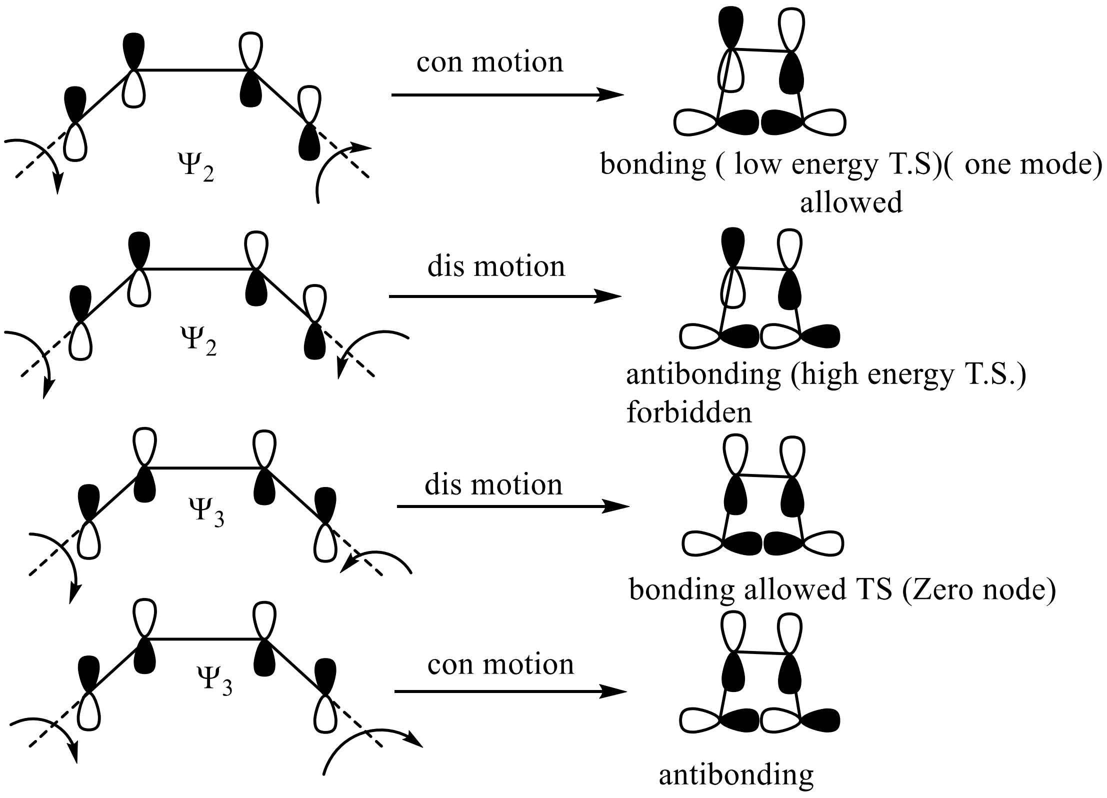


Fig: (**a**)= Thermal electrocyclization of 4npe conjugated system;
(**b**)= Photochemical electrocyclization of 4npe conjugated

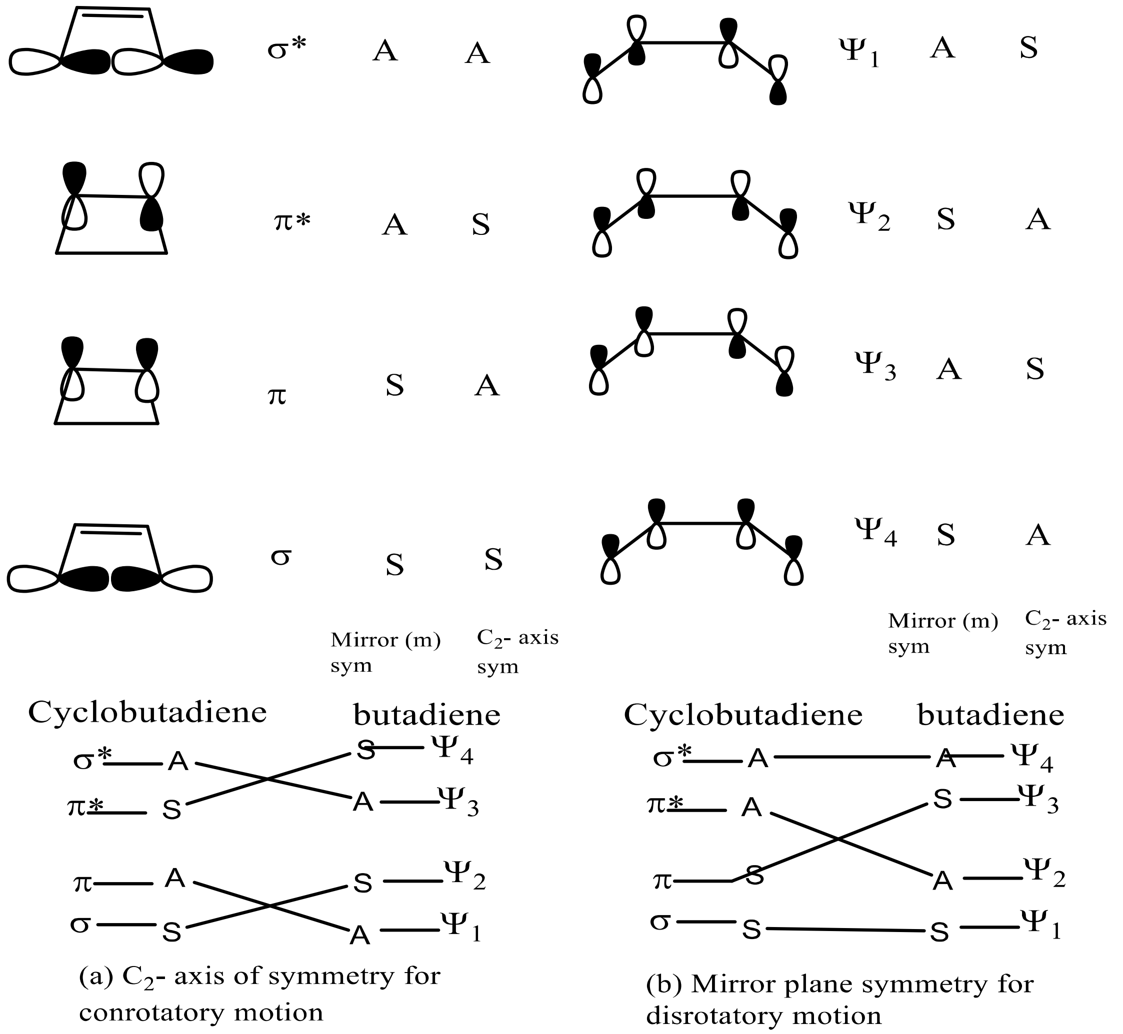
### 1.2.1. The Orbital Correlation Diagrams of Reactants and Products:

Longuet-Higgins and Abrahamson suggested that in any concerted process, the orbitals of the starting material and product have the same symmetry. This is also supported by Woodward and Hoffmann.

The cyclobutene–butadiene interconversion may be considered as an example to verify the fact by construction of a correlation diagram.

For cyclobutene, the bonding orbitals are σ and π, while the antibonding orbitals are σ* and π*.

For butadiene, the bonding orbitals are ψ₁ and ψ₂, and antibonding orbitals are ψ₃ and ψ₄. In thermal reaction, conrotatory ring opening of cyclobutene to butadiene, $C_2$ (twofold) axis of symmetry is maintained throughout the reaction, while for photochemical reaction, disrotatory ring opening, a mirror plane (m) symmetry is maintained throughout the reaction.



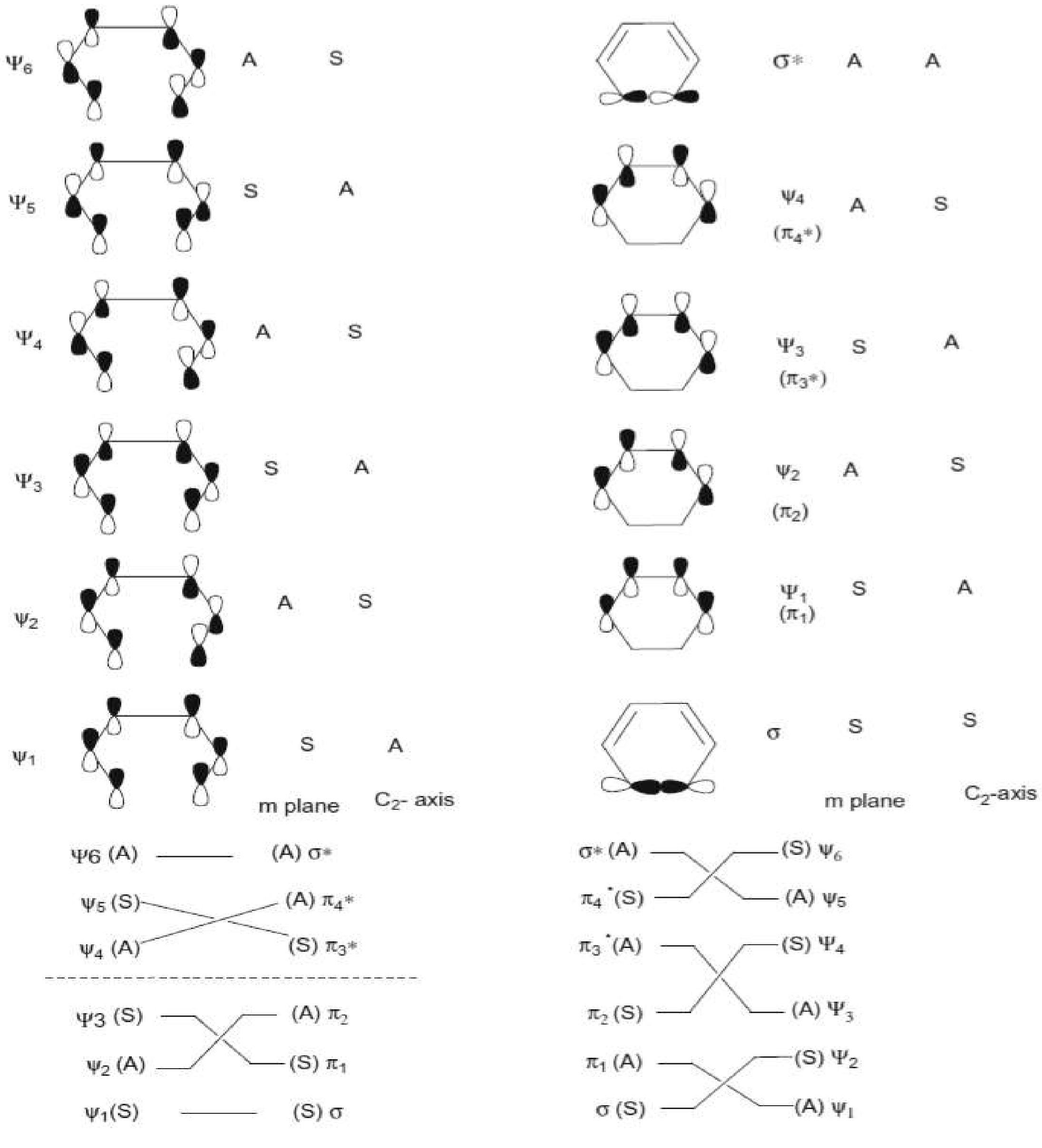
(a) $C_2$- axis of symmetry for conrotatory motion

(b) Mirror plane symmetry for disrotatory motion

(**a**)=C2-axis of symmetry is maintained in thermal conversion of cyclobutene to butadiene; (**b**)= mirror plane symmetry is maintained in photochemical conversion of cyclobutene to

Next, consider the thermal conversion of a 1,3,5-hexatriene to a 1,3-cyclohexadiene by the disrotatory motion where mirror (m)-symmetry is maintained in the orbitals of the reactant and product.

In photochemical conversion of 1,3-cyclohexadiene into 1,3,5-hexatriene or vice versa, the C2-axis of symmetry is maintained in conrotatory motion of the terminal groups.



(a) m plane classification

(b) C2 axis classification

**(a)**= Mirror plane (m) symmetry is maintained inthermal conversion of 1,3,5-hexatriene into 1,3-cyclohexadiene;

**(b)**= C2-axis of symmetry is maintained in photochemical conversion of 1,3-cyclohexadiene into 1,3,5-hexatriene or vice versa

### 1.2.2. Shortcut to Determine the Product in Electrocyclic Ring Openingand Ring Closing Reaction:

ring closing eletrocyclic reaction →

| Site of substituents | Con or Dis rotation | Geometry of substitution |
|---|---|---|
| O | D | C |
| O | C | T |
| S | C | C |
| S | D | T |

← ring opening eletrocyclic reaction

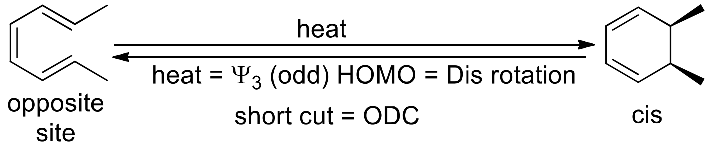
O = opposite site, S = same site, D = Dis rotation, C = Con rotation, T = trans, C = cis

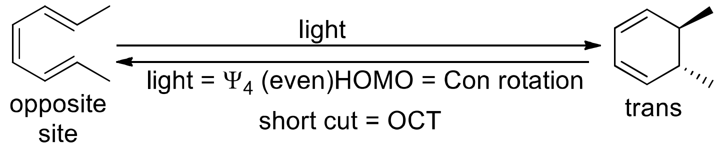
Even HOMO = Con rotatory Odd HOMO = Dis rotatory

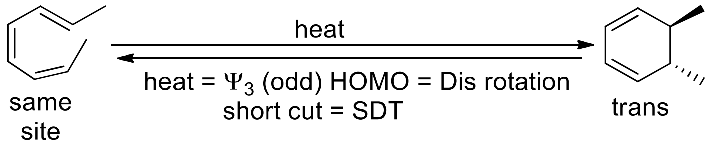
ZZ/EE= opposite site ZE/EZ= same site

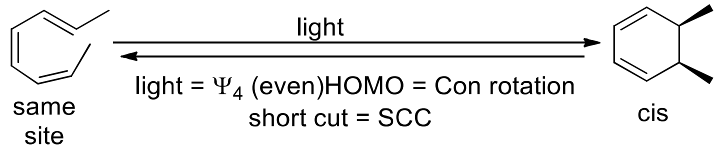
**Example:**

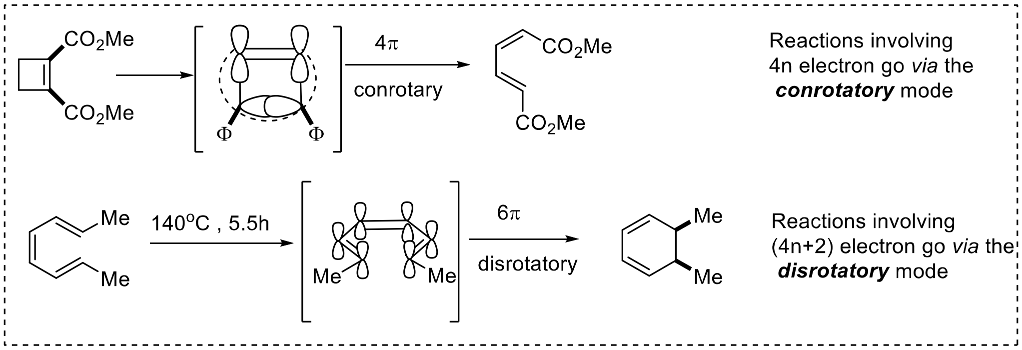
Ring opening and closing reaction:









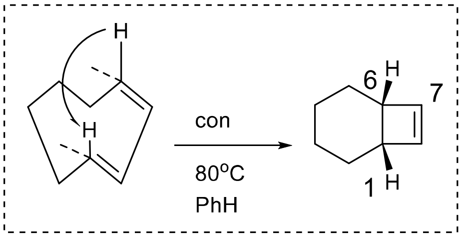


Reactions involving 4n electron go *via* the ***conrotatory*** mode

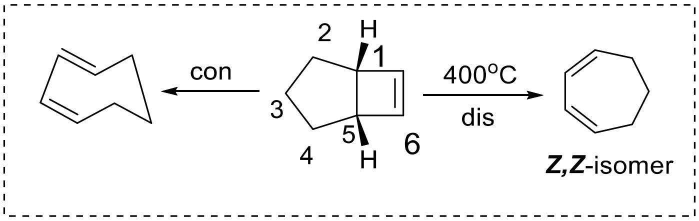
Reactions involving (4n+2) electron go *via* the ***disrotatory*** mode

### 1.2.3. Applications of Neutral Conjugated Systems in Electrocyclic Reactions:

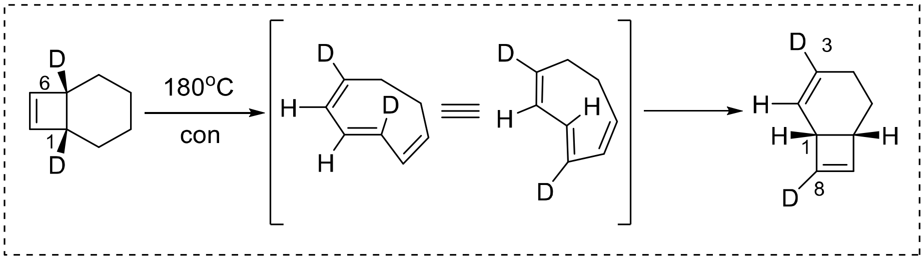
Electrocyclic reaction of E, Z-1, 3-cyclooctadiene leads to cis-bicyclo[4.2.0]- oct-7-ene because of strain associated with trans double bond.



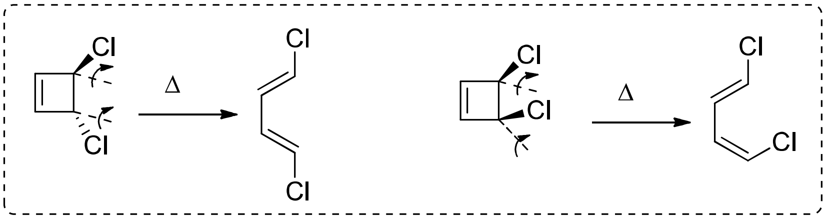
Although cyclobutenes are converted into butadienes on heating to get relief of ring strain, cis-bicyclo[3.2.0]-hept-6-ene on heating gave Z,Z-1,3-cycloheptadiene by forbidden disrotatory motion. This anomaly of the Woodward–Hoffmann rules can be accounted for by the stability of the product formed. In this case, allowed conrotatory motion gives the strained E,Z-1,3-cycloheptadiene, which is less stable due to ring strain and hence rapidly isomerizes to Z,Z-isomer at the reaction temperature in low yield.



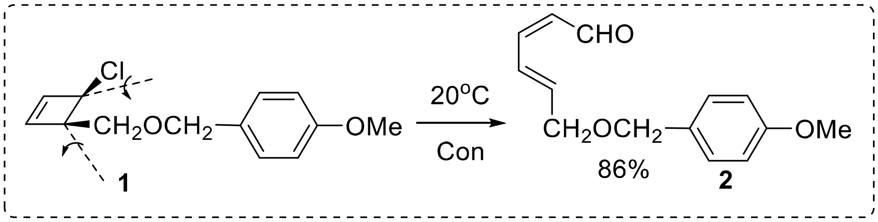
The thermal conversion of cis-1,6-dideuterio-bicyclo [4.2.0]- oct-2,7-diene to cis-3,8-dideuterio-isomer via trans-isomer.



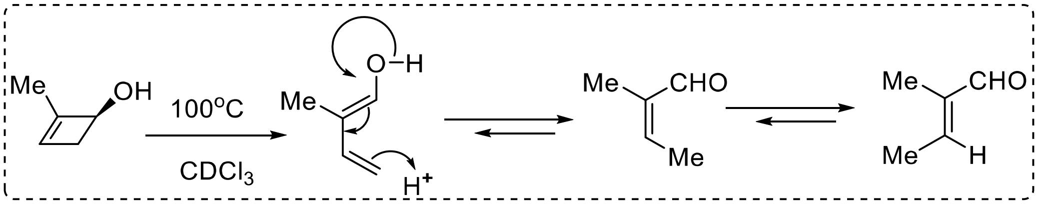
Study of the electrocyclic ring opening of cis- and trans-3,4-dichlorocyclobutenes indicated that trans-isomer reacts at lower temperature. This is due to ring opening by outward conrotatory motion of donor chlorine substituents while in case of cis-isomer, activation energy is higher as one of the chlorines rotates inward.



When a cyclobutene ring contains both electron-donating and electron-accepting substituents, conrotatory outward or inward motion of the substituents depends on the size of the substituents.

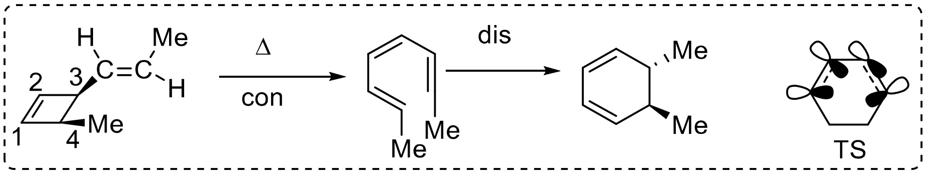


3-Hydroxy-2-methylcyclobutene on electrocyclic ring opening undergoes keto-enol tautomerization to afford the product.



Cyclobutene 9 having olefinic function at C-3 or C-4 position undergoes inward ring opening from the olefinic substituent site followed by ring closure to give the product.

This inward motion of the olefinic substituent stabilizes the HOMO of the TS by π-orbital interaction of the substituent with the donor lobes of p-orbitals of the breaking σ bond of the ring carbons.



### 1.2.4. Examples:

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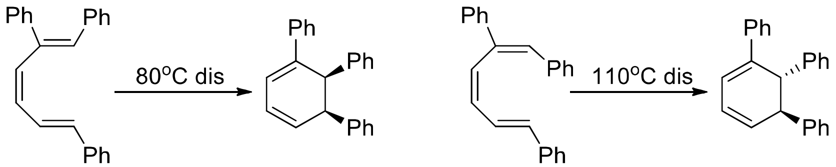

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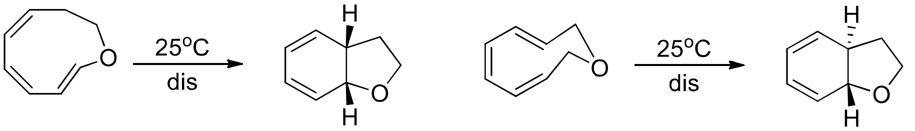

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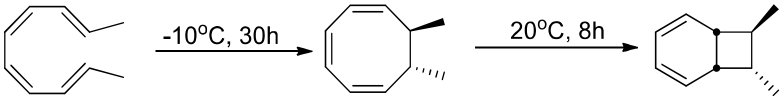

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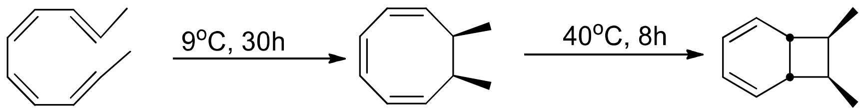

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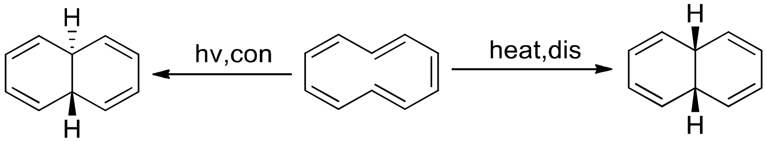

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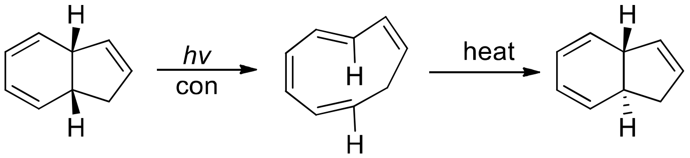

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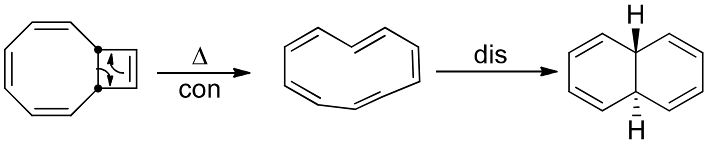

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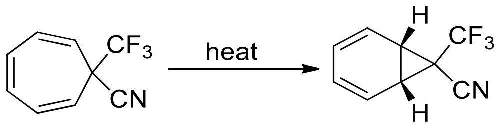

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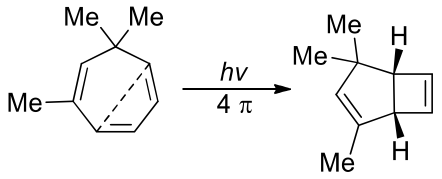

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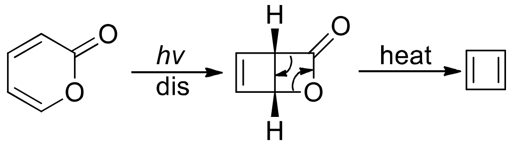

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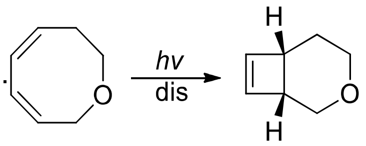

12.