**M.Sc. Semester-IV**
**Core Course-9 (CC-9)**
**Synthetic Organic Chemistry**

# II. Pericyclic Reactions

## 6. Diels-Alder Reaction


**Dr. Rajeev Ranjan**
**University Department of Chemistry**
**Dr. Shyama Prasad Mukherjee University, Ranchi**

**II Pericyclic Reactions 20 Hrs**

Molecular orbital symmetry, Frontier orbitals of ethylene, 1,3-butadiene, 1, 3, 5-hexatriene, allyl system, Classification of pericyclic reactions. FMO approach, Woodward-Hoffman correlation diagram method and PMO approach for pericyclic reaction under thermal and photochemical conditions.

Electrocyclic reactions: Conrotatary and disrotatary motion, 4n and (4n+2) systems, Cycloaddition reaction: [2+2] and [4+2] cycloaddition reaction, Cycloaddition of ketones, Secondary effects in [4+2] cycloaddition. Stereochemical effects on rate of cycloaddition reaction, Diels-Alder reaction, 1,3-dipolar cycloaddition, Chelotropic reaction, The Nazarov reaction.

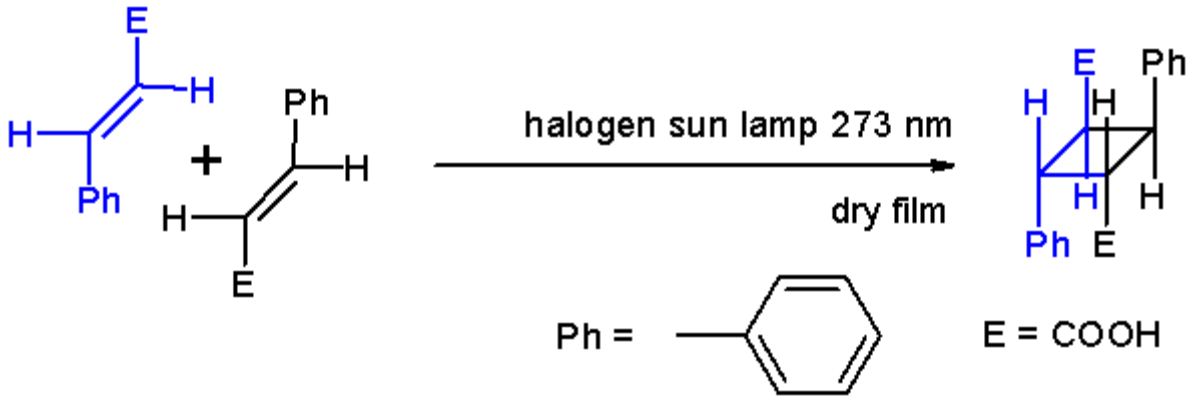
Sigmotropic rearrangement: Suprafacial and antarafacial shift involving H and carbon-moieties, Peripatetic cyclopropane bridge, Retention and inversion of configuration, [3,3]-, [1,5]-, [2,3]-, [4,5]-, [5,5]-, and [9,9]-Sigmatropic rearrangements, Claisen rearrangements (including Aza-Claisen, Ireland-Claisen), Cope rearrangements (including Oxy-Cope, Aza-Cope), Sommelet-Hauser rearrangements, Group transfer reaction, Ene reaction, Mislow - Evans rearrangement, Walk rearrangement.

**Coverage:**

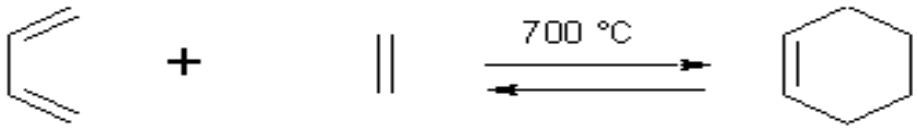
1. Cycloaddition Reaction: [4+2] and [2+2] Cycloaddition Reactions
2. [4+2]-Cycloaddiitions of Propenyl System
3. Diels-Alder Reaction
4. Secondary Effects in [4+2] Cycloaddition
5. Selection Rules for Cycloadditions.

# Cycloaddition Reaction

A **cycloaddition** is a reaction, in which two π bonds are lost and two σ bonds are gained. The resulting reaction is a cyclization reaction.

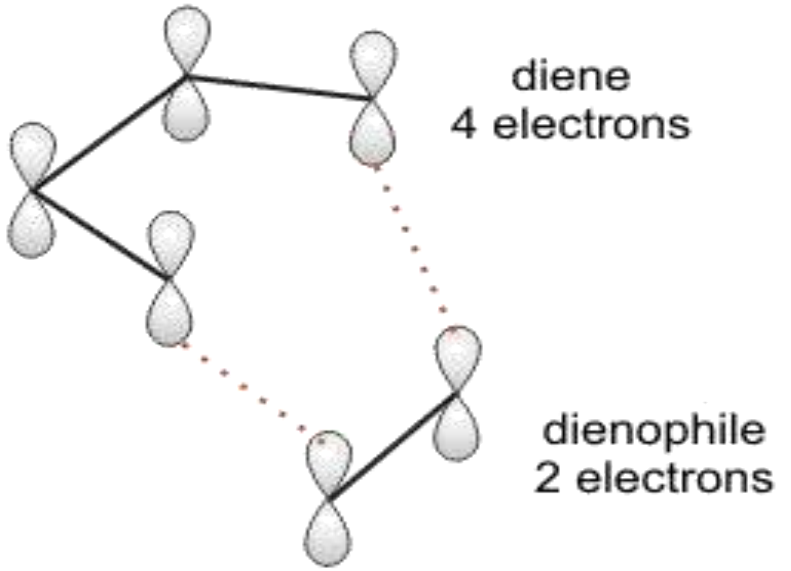


# 4+2 Cycloaddition Reaction
# (Supra-Supra)




The Diels-Alder reaction represents the prototype of cycloadditions. Besides the Grignard reaction, it is the most cited name reaction in chemical literature.

The reaction principle was discovered in 1928 by **Otto Diels** and his student **Kurt Alder**. Both were honored with the Nobel Prize for Chemistry in 1950.



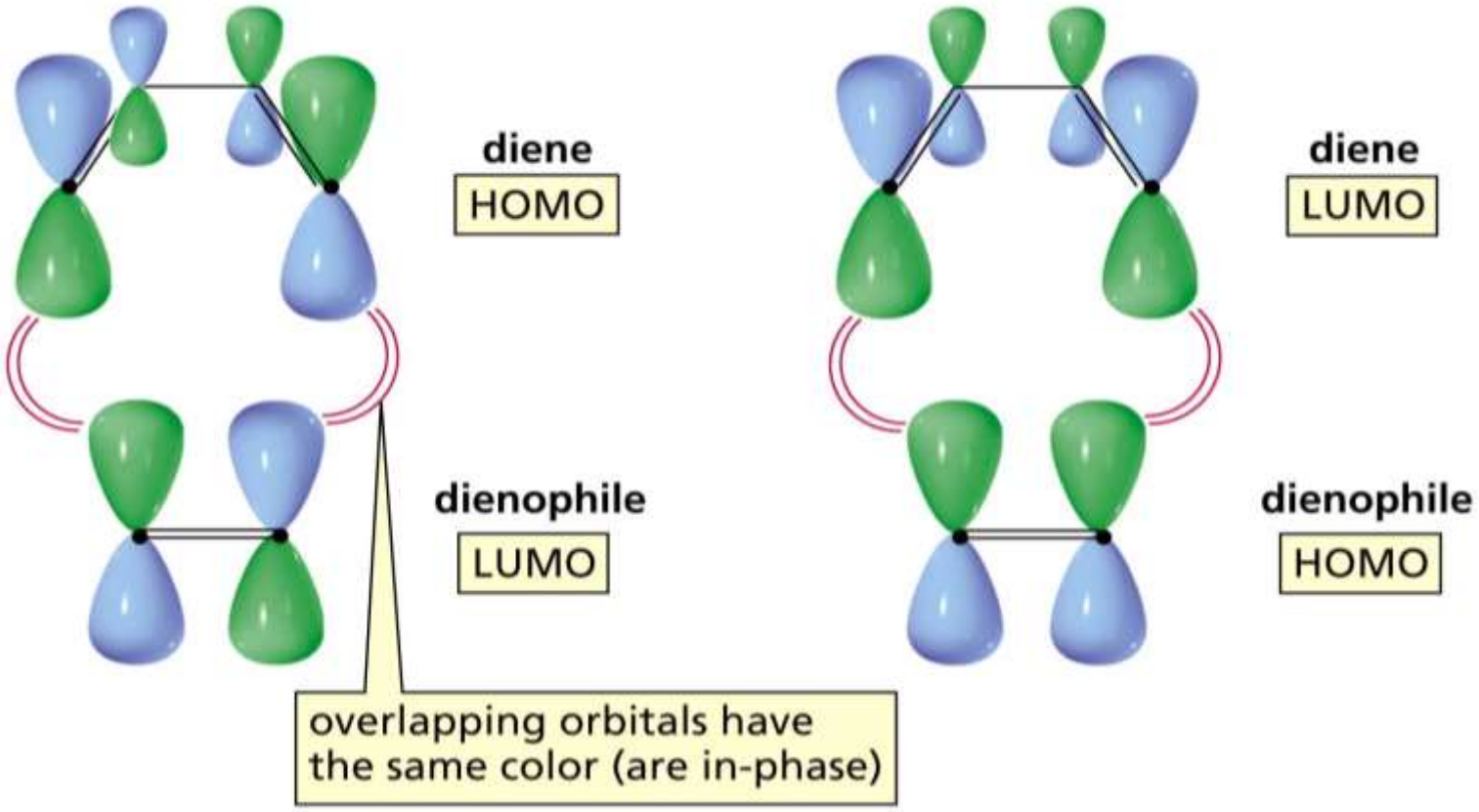
**Otto Diels**
1876-1954

**Kurt Alder**
1902-1958

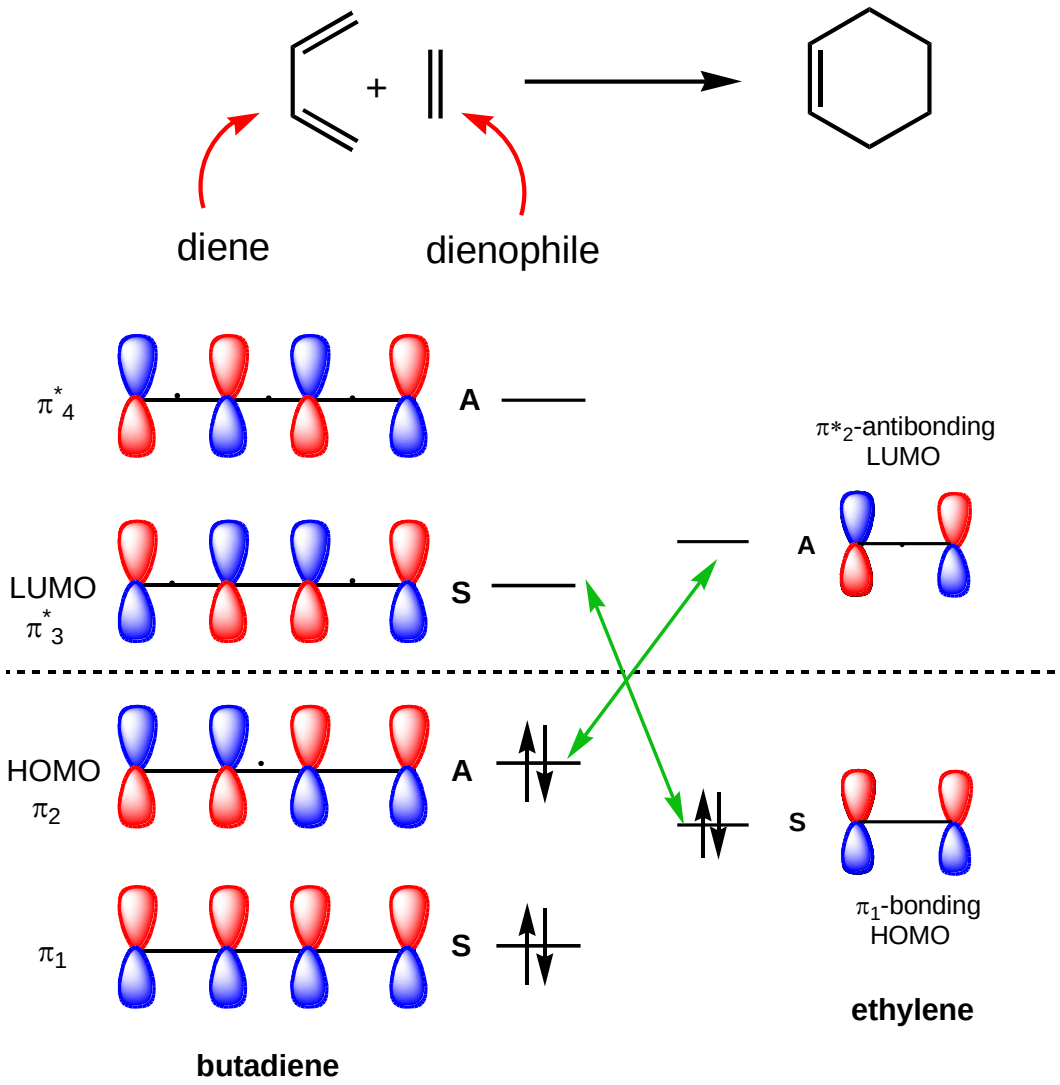
The reaction principle was discovered in 1928 by **Otto Diels** and his student **Kurt Alder**. Both were honored with the Nobel Prize for Chemistry in 1950.

The Diels-Alder reaction represents the prototype of cycloadditions. Besides the Grignard reaction, it is the most cited name reaction in chemical literature.

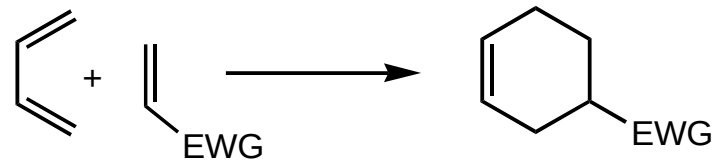
# Diels-Alder Cycloaddition : Frontier Orbital Intractions
## 6-e, 4+2 Supra-supra



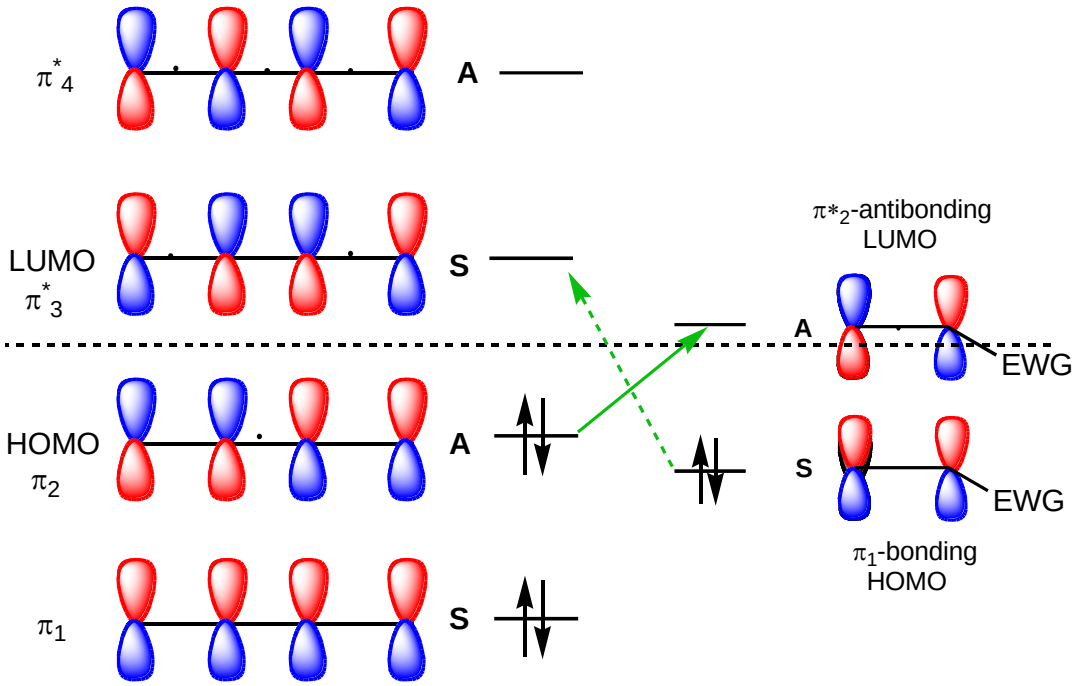
# Diels-Alder Reaction
# An Allowed [4+2] Cycloaddition



# Diels-Alder Reaction:
# The Effect of Electron Withdrawing Groups

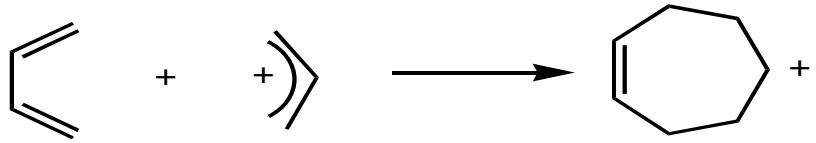


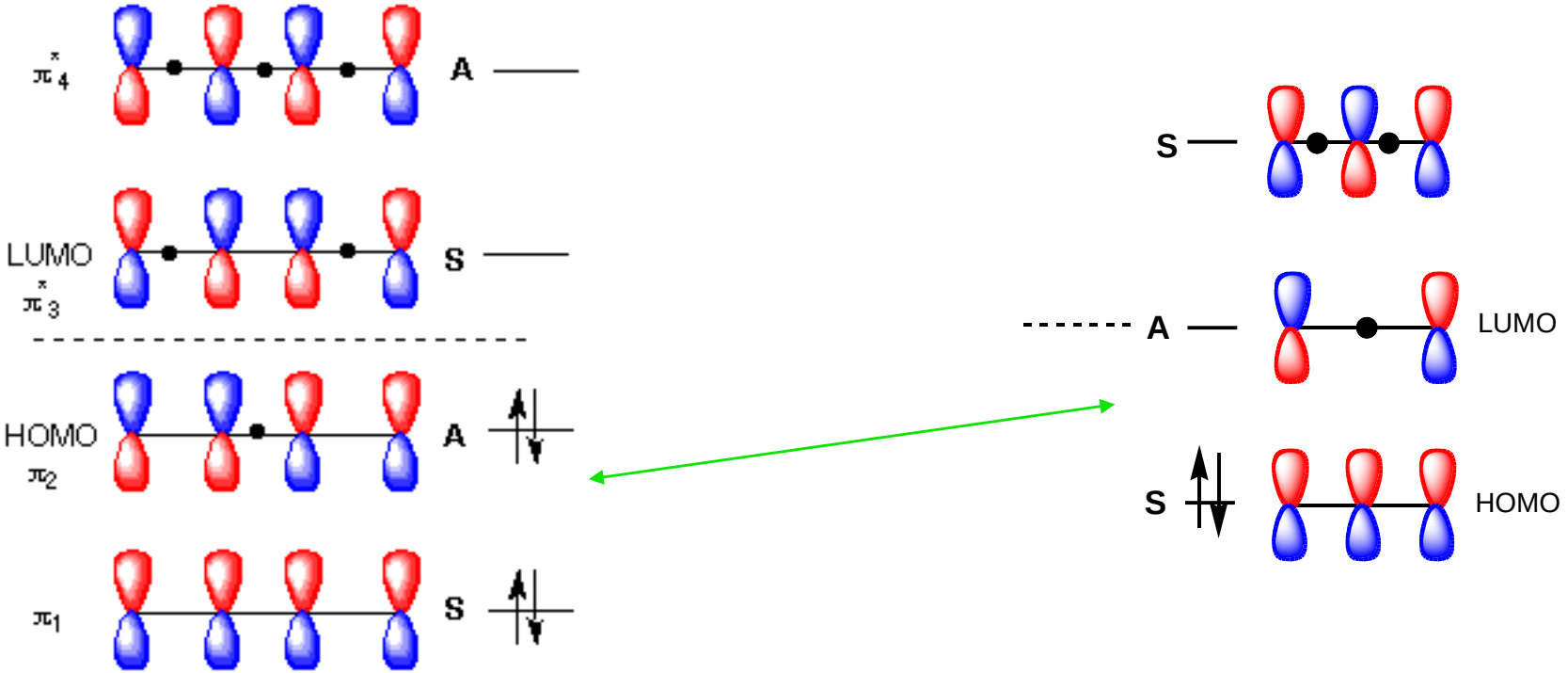

diene dienophile



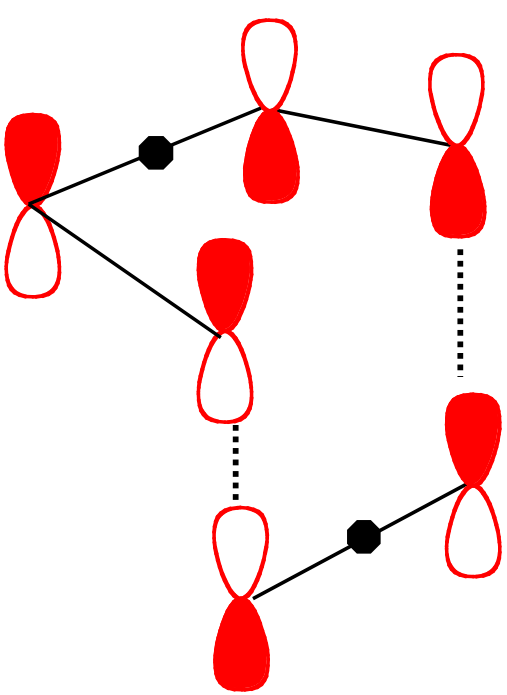

**butadiene** **deactivated ethylene**

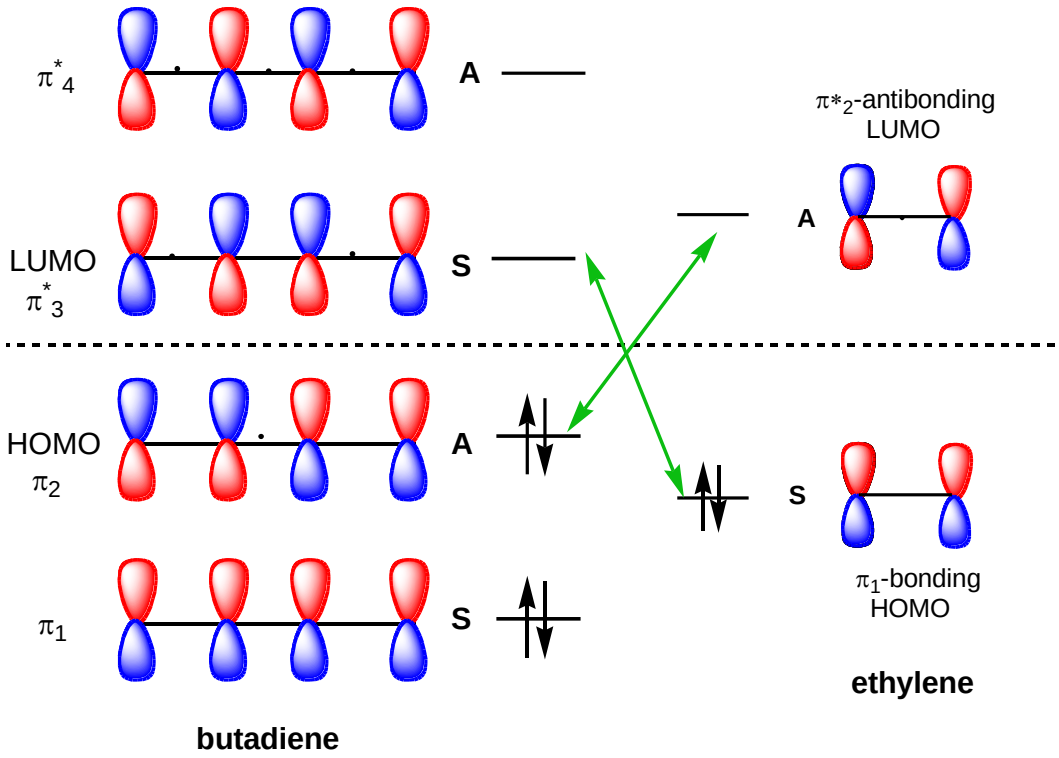
# [4+2]-Cycloaddiitions of Propenyl System



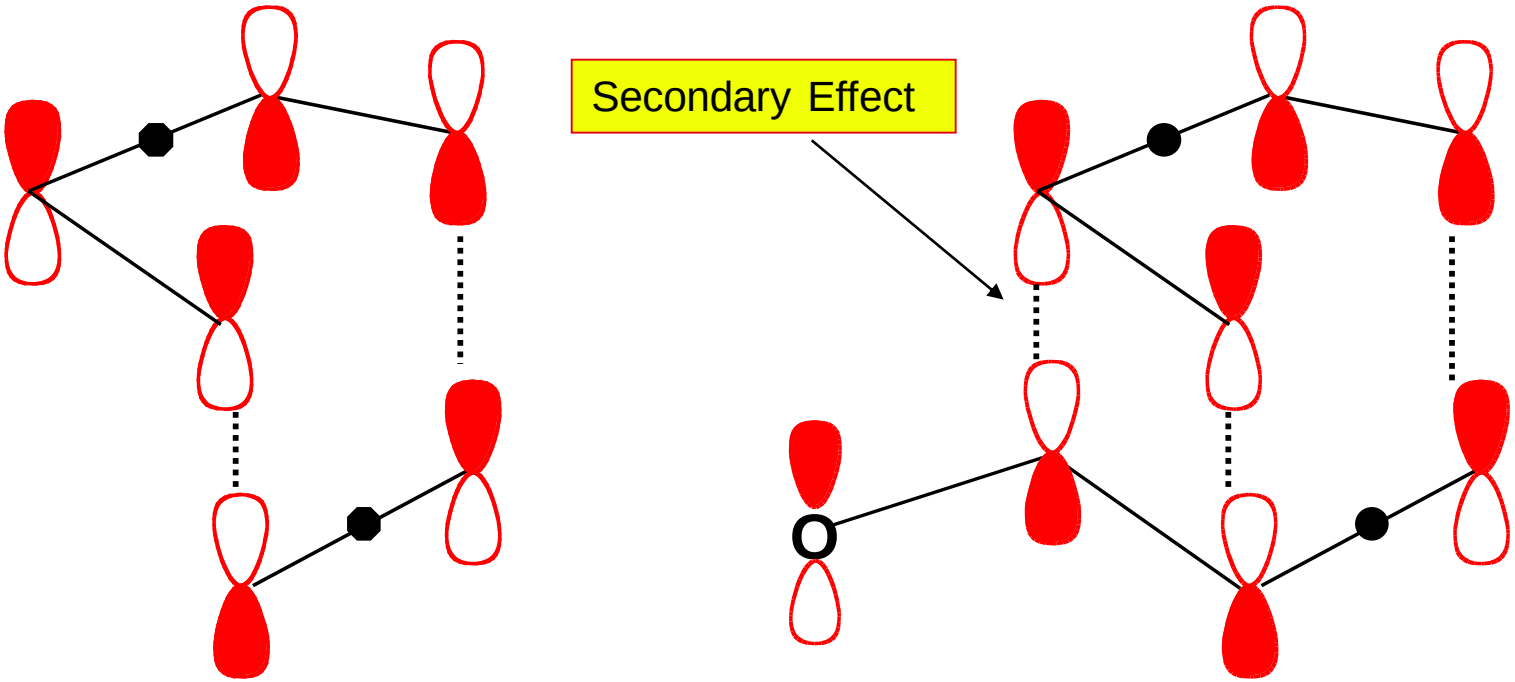


# Diels-Alder Reaction: Mechanism

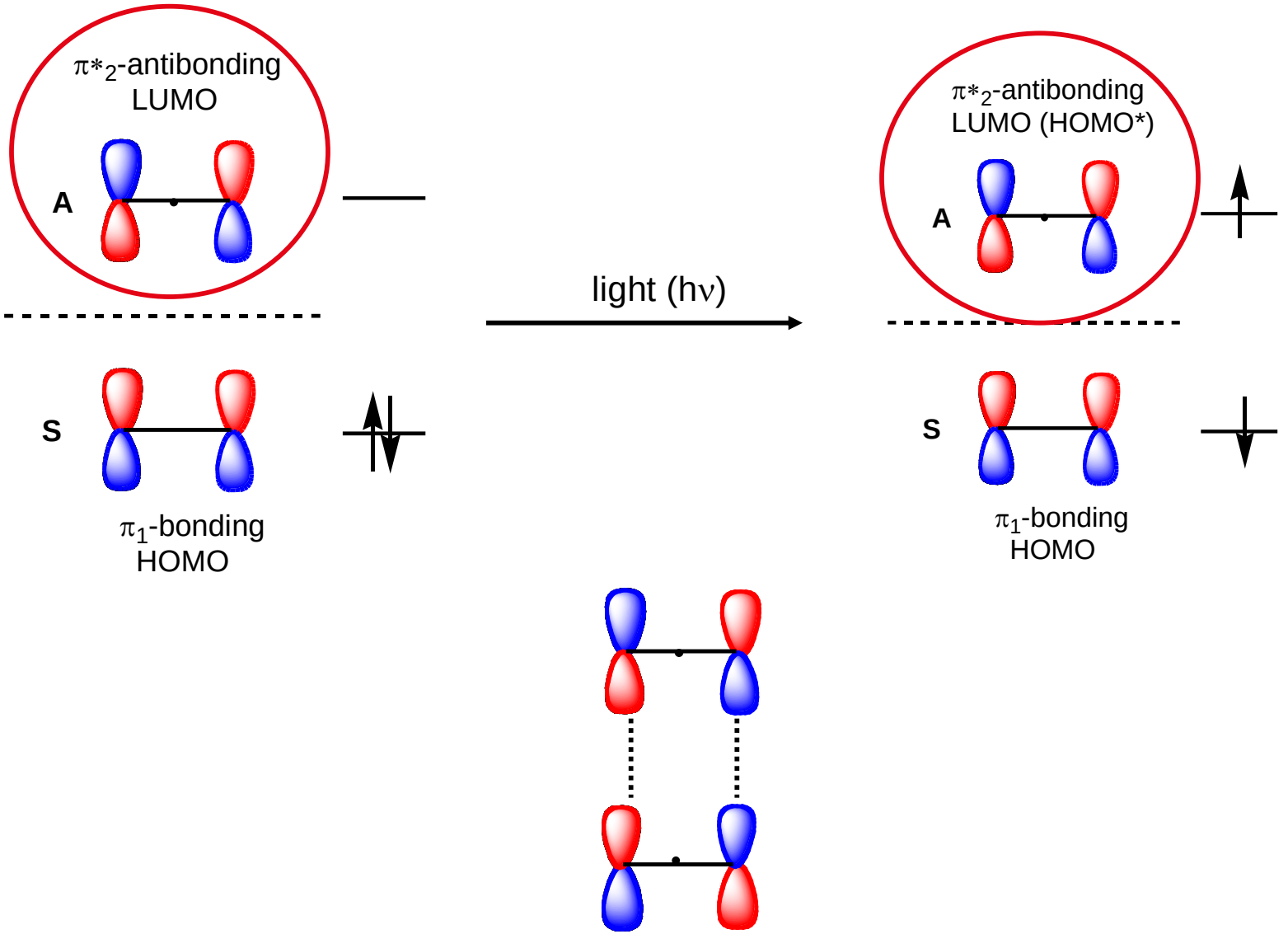




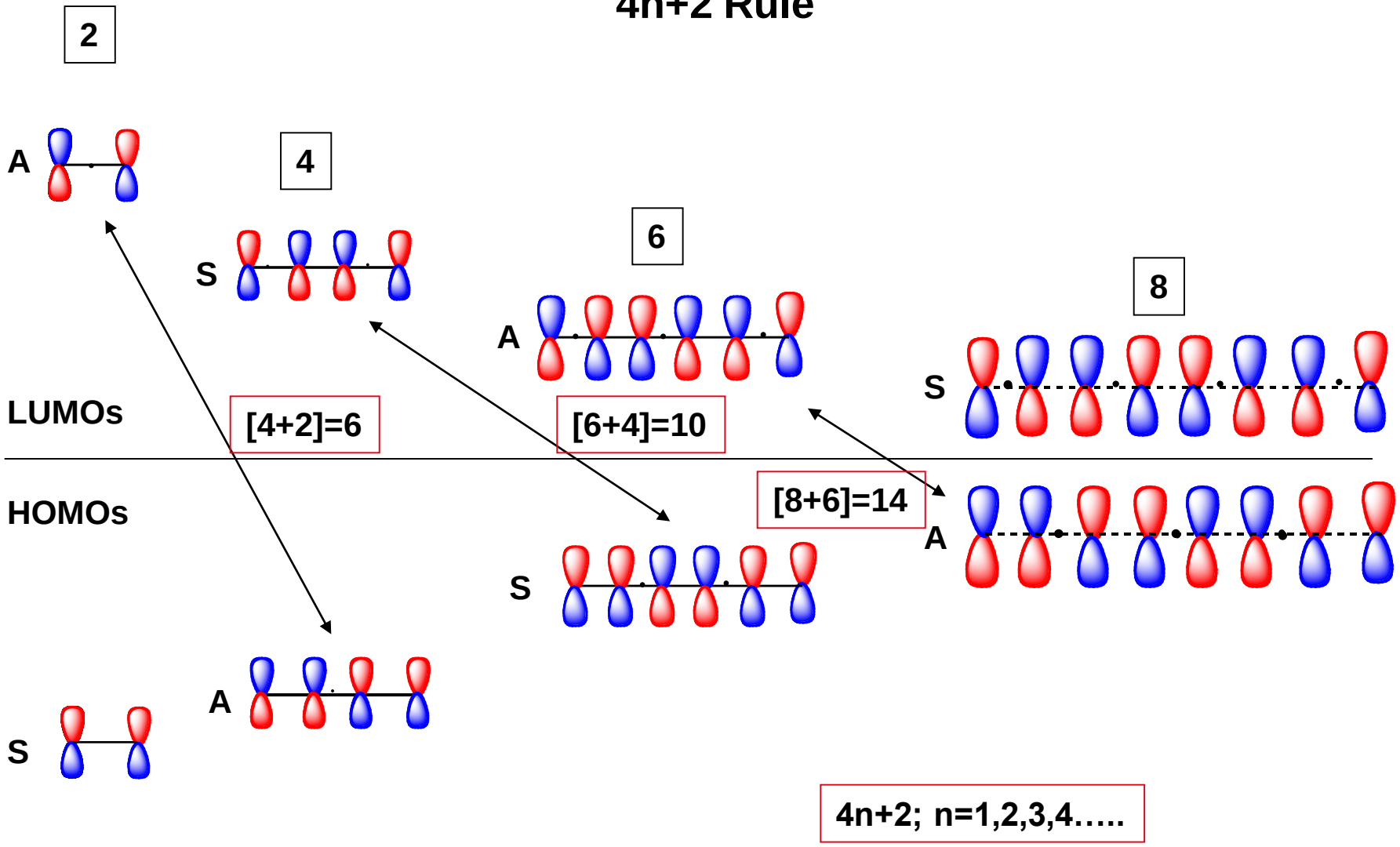
# Diels-Alder Reaction: The Endo Effect



# A [2+2] Cycloaddition Reaction

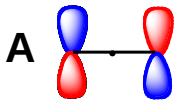


# Thermally Allowed Cycloadditions : Selection Rule
# 4n+2 Rule

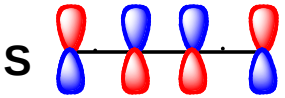


# Photochemically Allowed Cycloadditions :Selection Rule
## 4n Rule

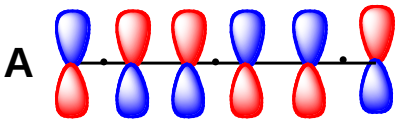
2 [2+2]=4



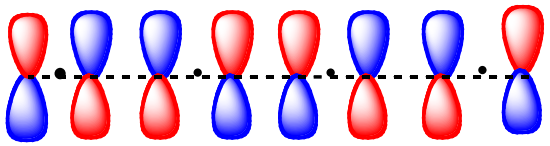

4 [4+4]=8




6 [6+6]=12



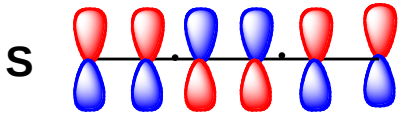

8 [8+8]=16

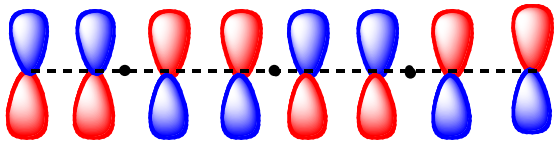


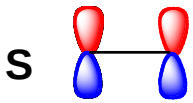

**LUMOs**

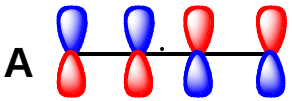
---

**HOMOs**




4n; n=1,2,3,4…..

and [2+6]=8; [8+4]=12

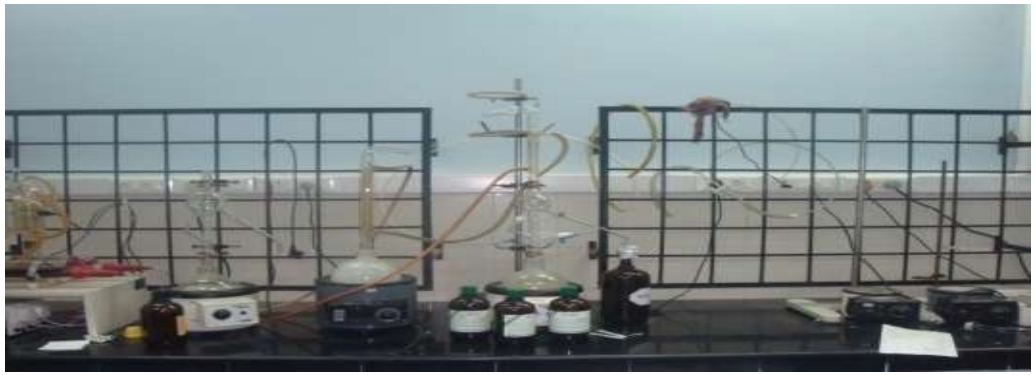
# Summary of Selection Rules of Cycloadditions

**Thermal 4n+2**

**Photochemical 4n**

| | 2 | 4 | 6 | 8 | 10 |
|---|---|---|---|---|---|
| 2 | P | T | P | T | P |
| 4 | T | P | T | P | T |
| 6 | P | T | P | T | P |
| 8 | T | P | T | P | T |
| 10 | P | T | P | T | P |

# Thank You



**Dr. Rajeev Ranjan**
**University Department of Chemistry**
**Dr. Shyama Prasad Mukherjee University, Ranchi**