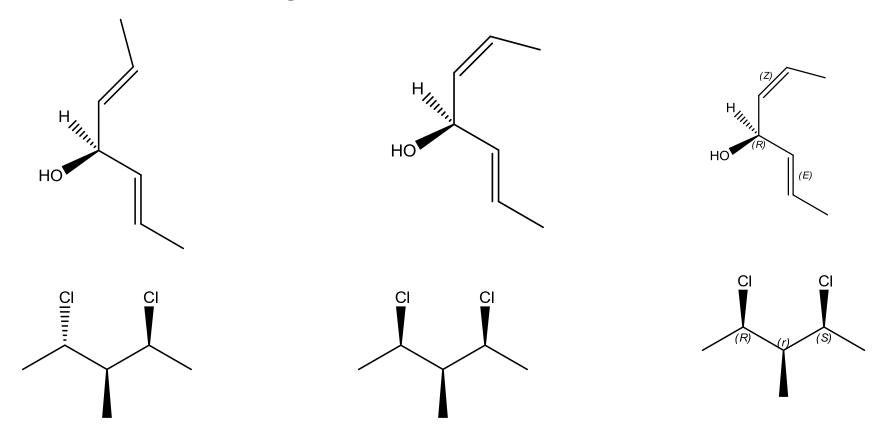
Additional Information on Relative Priority

Pericyclic Reaction



group with descriptor 'R' has priority over its enantiomorph 'S' and group with Z or Cis descriptor has priority over E or trans

### pseudo-asymmetric carbon atom

The tetrahedrally coordinated carbon atom bonded to four different entities, two of which have the same constitution but opposite chirality sense

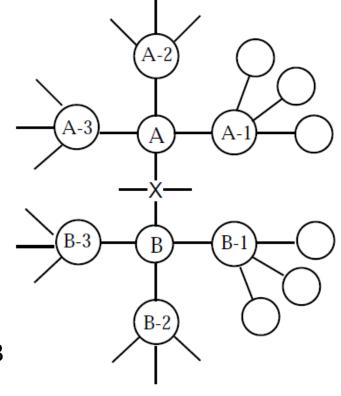
Compare the highest priority atoms, i.e. compare A-1 with B-1.

If A-1 is a higher priority atoms than B-1, then A is higher priority than B

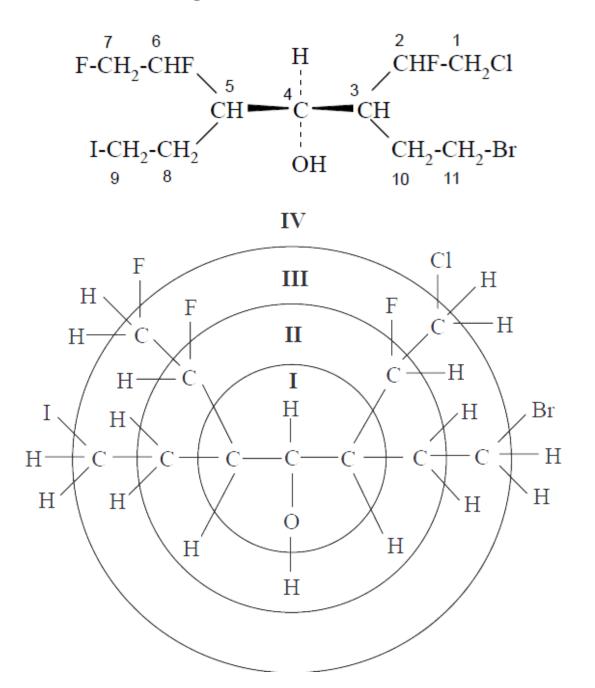
If A-1 and B-1 are the same atom, then compare the second highest priority atoms directly bonded to A and B (A-2 with B-2)

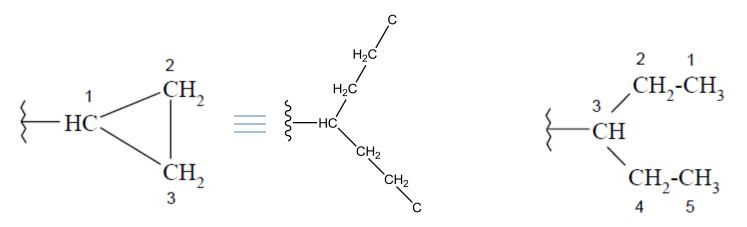
if A-2 is a higher priority atom than B-2, then A is higherpriority than B.

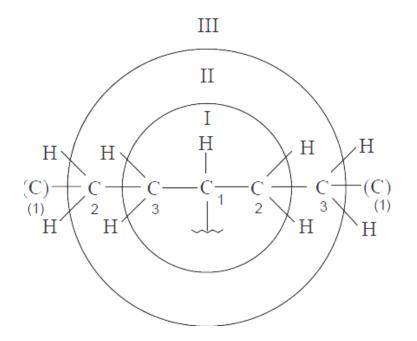
If A-2 and B-2 are identical atoms, compare A-3 with B-3

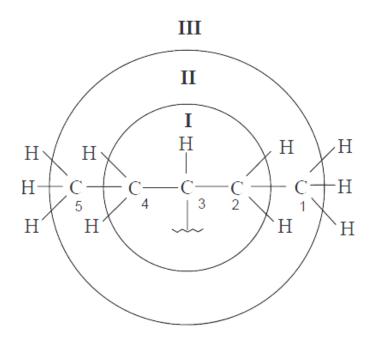


If a difference still can not be found, move out to the next highest priority group (A-1 and B-1 in the diagram) and repeat the process

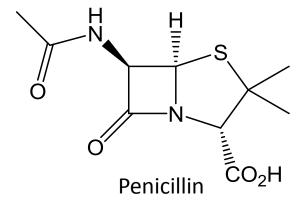








Provide the stereo-descriptor for the chiral centers of Penicillin



# **Pericyclic Reactions**

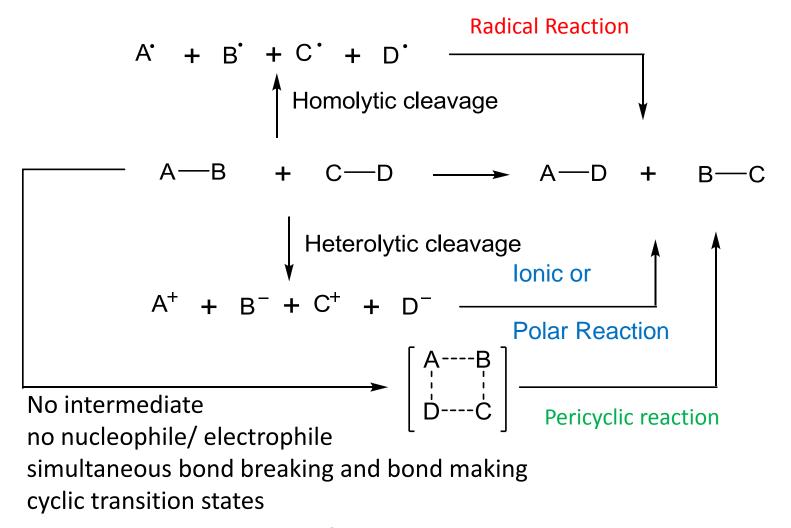
Books: Any organic chemistry book

Lectures mainly follow:

Organic Chemistry by P. Y. Bruice
Organic Chemistry by J. Clayden, N. Greeves and S. Warren

**Advanced studies: Pericyclic Reactions by Ian Fleming** 

# **Organic Reactions**



Organic reactions are of three kinds

- Ionic or Polar Reaction
- 2. Radical Reaction
- 3. Pericyclic reaction

### Ionic or Polar Reaction

Reaction involving charged species; the product is formed combining Electrophiles and nucleophiles

### Ionic or Polar Reaction

Ionic reaction involves: ions as intermediates reaction between nucleophile and electrophile

### Radical Reaction

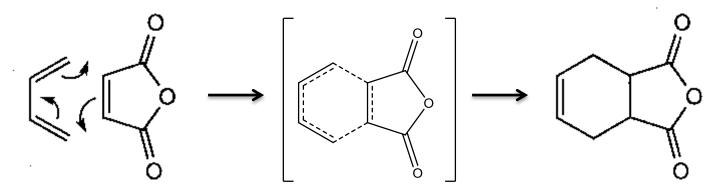
Reactions involving neutral radical intermediates are called radical reaction

$$CH_4 + Cl_2 + energy \longrightarrow CH_3Cl + CH_2Cl_2 + CHCl_3 + CCl_4 + HCl_3$$

### **Pericyclic Reactions**

Pericyclic reaction are those which are:

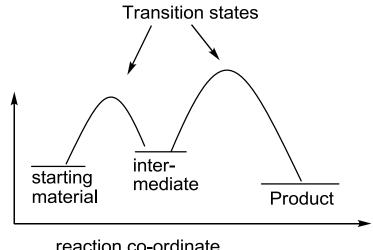
- 1. Concerted reaction with cyclic transition states
- 2. Without formation of intermediate
- Having simultaneous bond-forming and bond breaking process



#### **Concerted reaction**

# Transition state Energy Energy starting product material reaction co-ordinate

#### multistep lonic or radical reaction



reaction co-ordinate

### **Pericyclic Reactions: Classification**

### Types of pericyclic reaction:

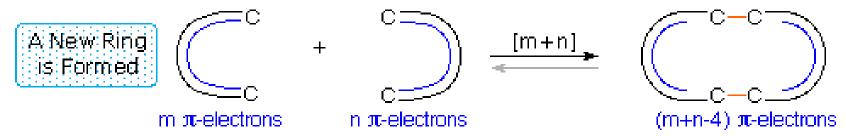
- a) Cycloaddition reaction
- b) Electrocyclic Reaction (electrocyclic ring closing and electrocyclic ring openning)
- c) Sigmatropic rearrangement
- d) Group transfer reaction

## **Pericyclic Reactions: Cycloaddition Reaction**

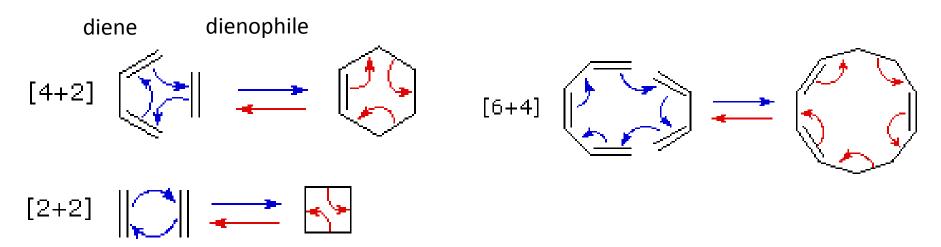
Cycloaddition reaction is characterized by

- a. two (or more) components reacting together
- b. to form **two (or more) new \sigma-bonds** at the end of both the  $\pi$ -components
- c. forming a ring
- d. with a reduction in the length of the conjugated system in each components.

### Cycloaddition Reactions



Note that two  $\pi$ -bonds are converted to two  $\sigma$ -bonds



# **Pericyclic Reactions: Cycloaddition Reaction**

How to assign the relative Stereochemistry?

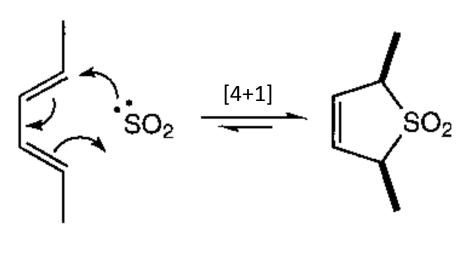
[4+2] under thermal condition

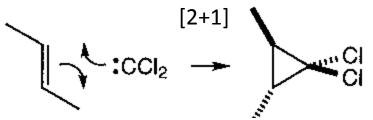
[2+2] in presence of light

reaction occurs at low temperature and short time

reaction require high temperature and longer time

### **Pericyclic Reactions: Cheletropic Reactions**





- **a. two components** reacting together
- b. to form **two new \sigma-bonds** at the end of both the  $\pi$ -components
- c. forming a ring
- d. with a reduction in the length of the conjugated system in each components.

Cheletropic reactions are a special type of cycloaddition/cycloreversion reactions

Two bonds are formed or broken at a single atom

The nomenclature for cheletropic reactions is the same as for cycloadditions

### **Looking forward**

**Pericyclic Reaction** 

Quize on 27th Aug: physical, inorganic and organic

Course material will be uploaded after 17:00 h on every Thursday @

http://www.iitg.ac.in/ckjana/ckjana/Teaching.html