Chelotropic reaction and Sigmatropic rearrangement

For Sem-V students
(CC12, Organic chemistry)

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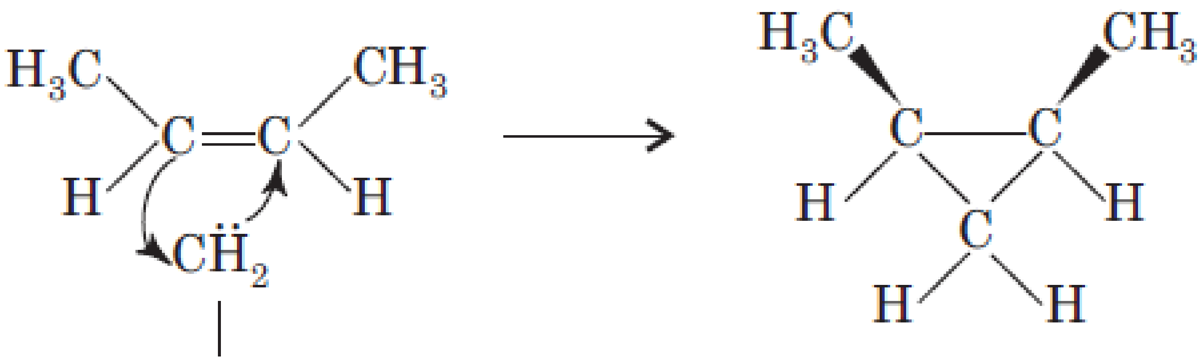
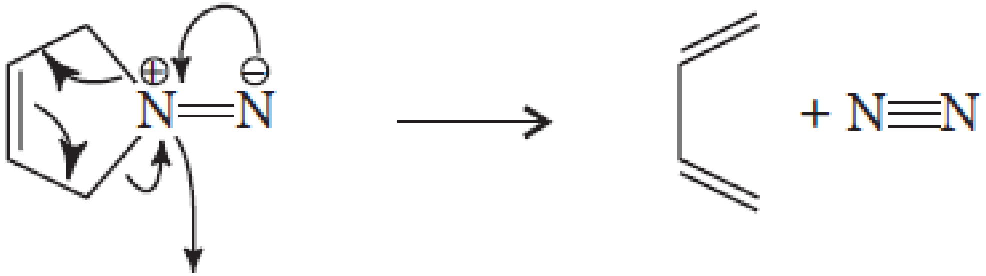
Chelotropic Reaction:

Chelotropic reactions are those reactions in which two σ bonds are formed on same atom or two σ bonds are broken on same atom.

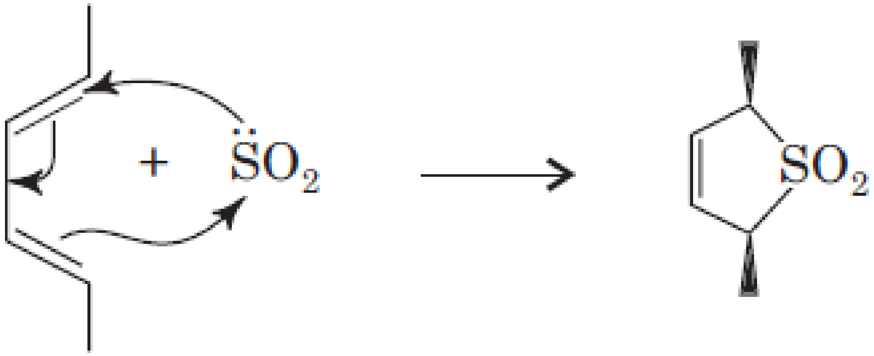
Intrusion & extrusion…



Two σ bonds are formed on this carbon in the product.



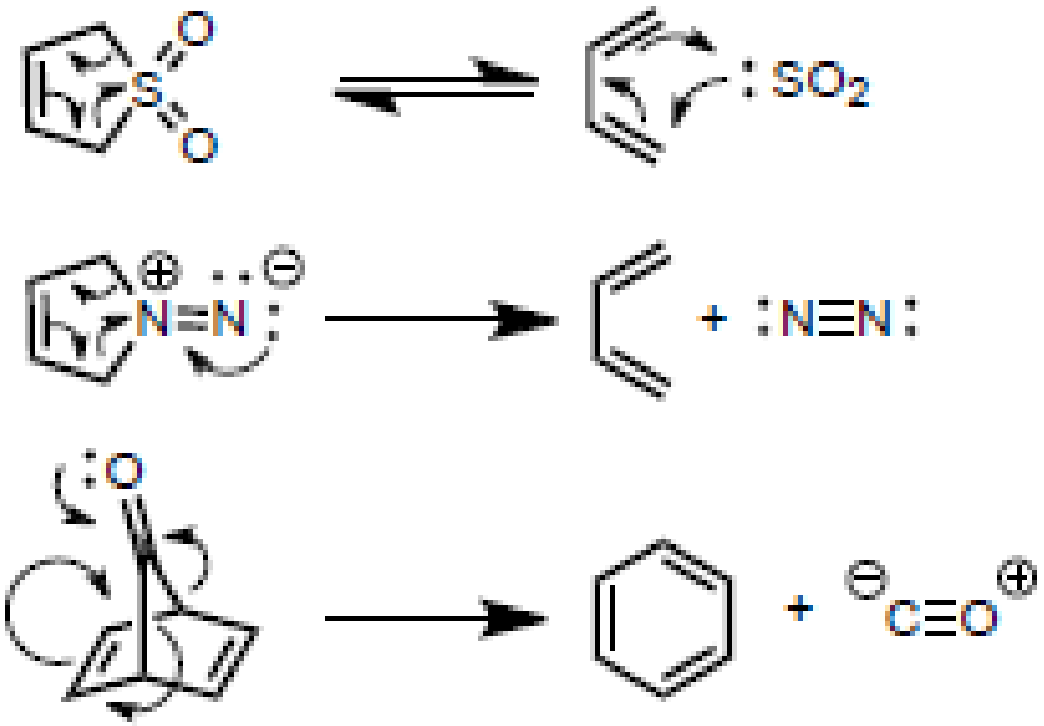
Two σ bonds are broken on nitrogen



Two σ bonds are formed on sulphur

Few more examples…….

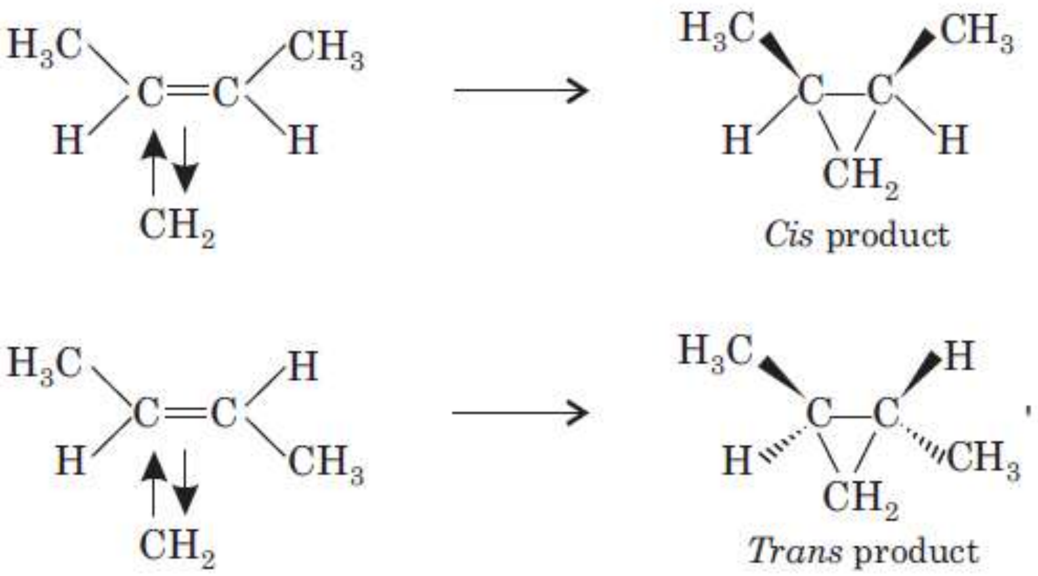
Extrusion……



[2 + 2] Chelotropic Cycloadditions:

A. Chelotropic Reactions of Alkenes with Singlet Carbenes

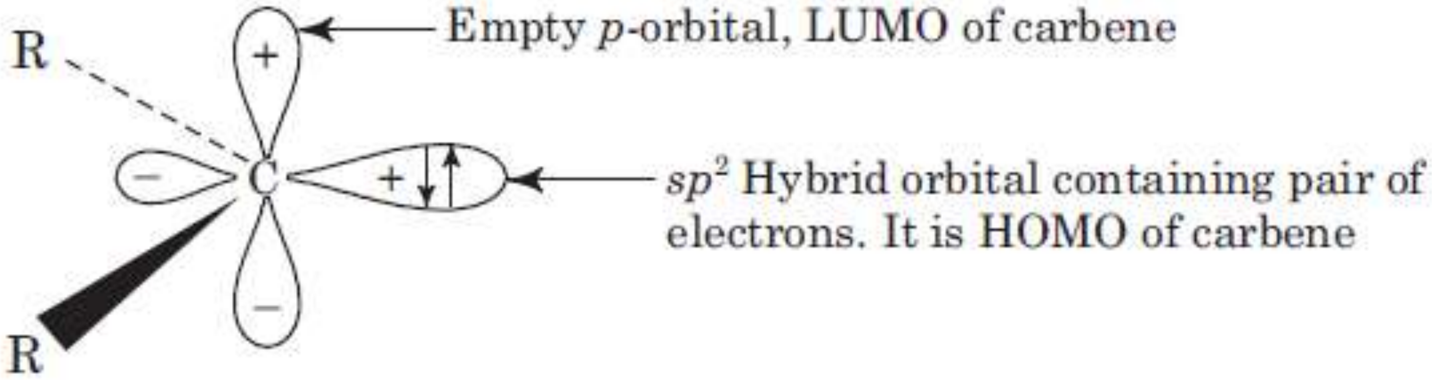
- Alkene reacts with carbene to form cyclopropane or substituted cyclopropane.
- This addition reaction is stereospecific with singlet carbenes.
- Reaction is thermal allowed reaction.



- The reaction is concerted reaction
- A bonding overlap between HOMO of a carbene and LUMO of an alkene or LUMO of carbene and HOMO of alkene is possible

Singlet carbene:

- Singlet carbenes have an unoccupied p orbital and two non-bonding electrons in the σ orbital.
- Only singlet carbenes can participate in cheletropic reactions
- Singlet carbene has three sp2 hybrid orbitals and one empty p-orbital perpendicular to the plane defined by the carbon atom and the two substituents on it.
- Out of three sp2 hybrid orbitals two are bonding and one is non-bonding having two electrons in it



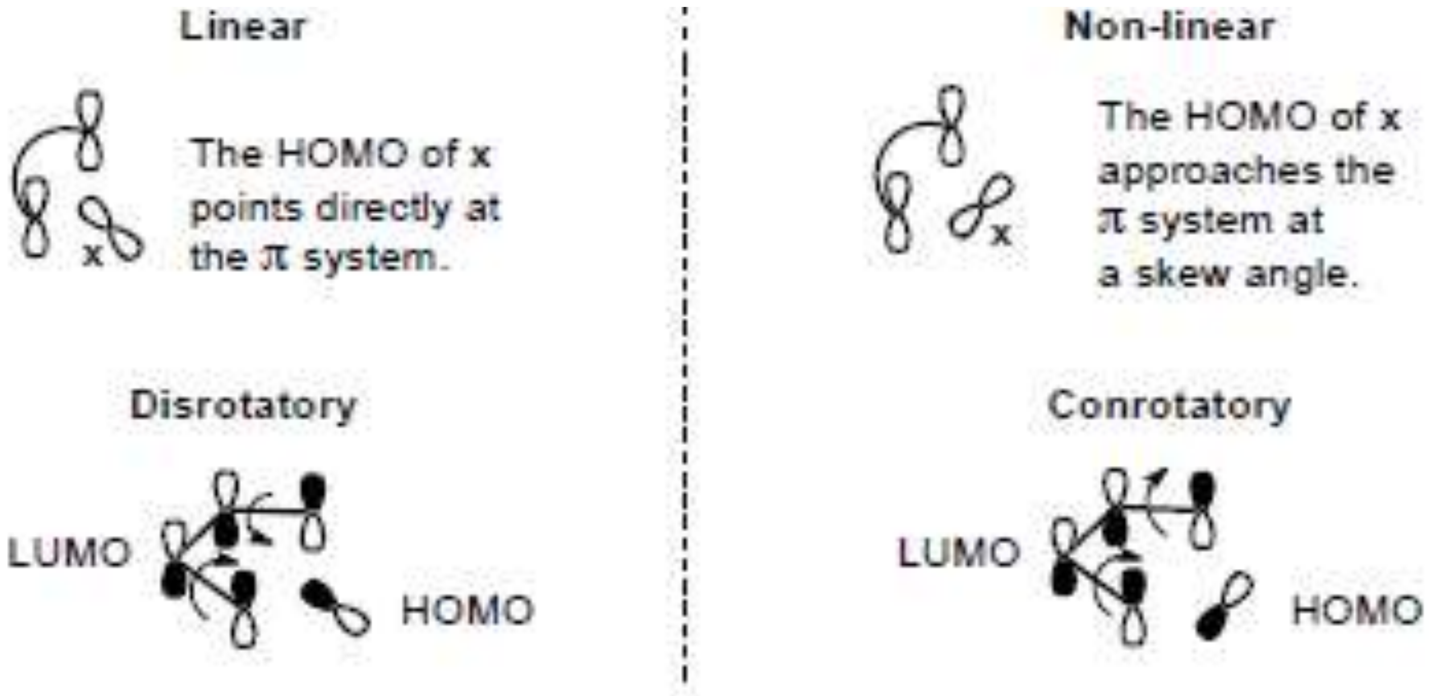
- Concerted cycloaddition reaction between alkene and carbene is [2 + 2] cycloaddition reaction
- This reaction is possible only if the carbene approaches the alkene sideways so that the plane defined by the carbon atom and its two substituents parallels the plane of the alkene
- In this orientation, the empty p-orbital of the carbene pointing towards the electrons of the π bond of alkene

Mechanism of reaction:

Linear approach vs. Non-linear approach

- **Cheletropic reaction** analysis is typically done in the addition direction.

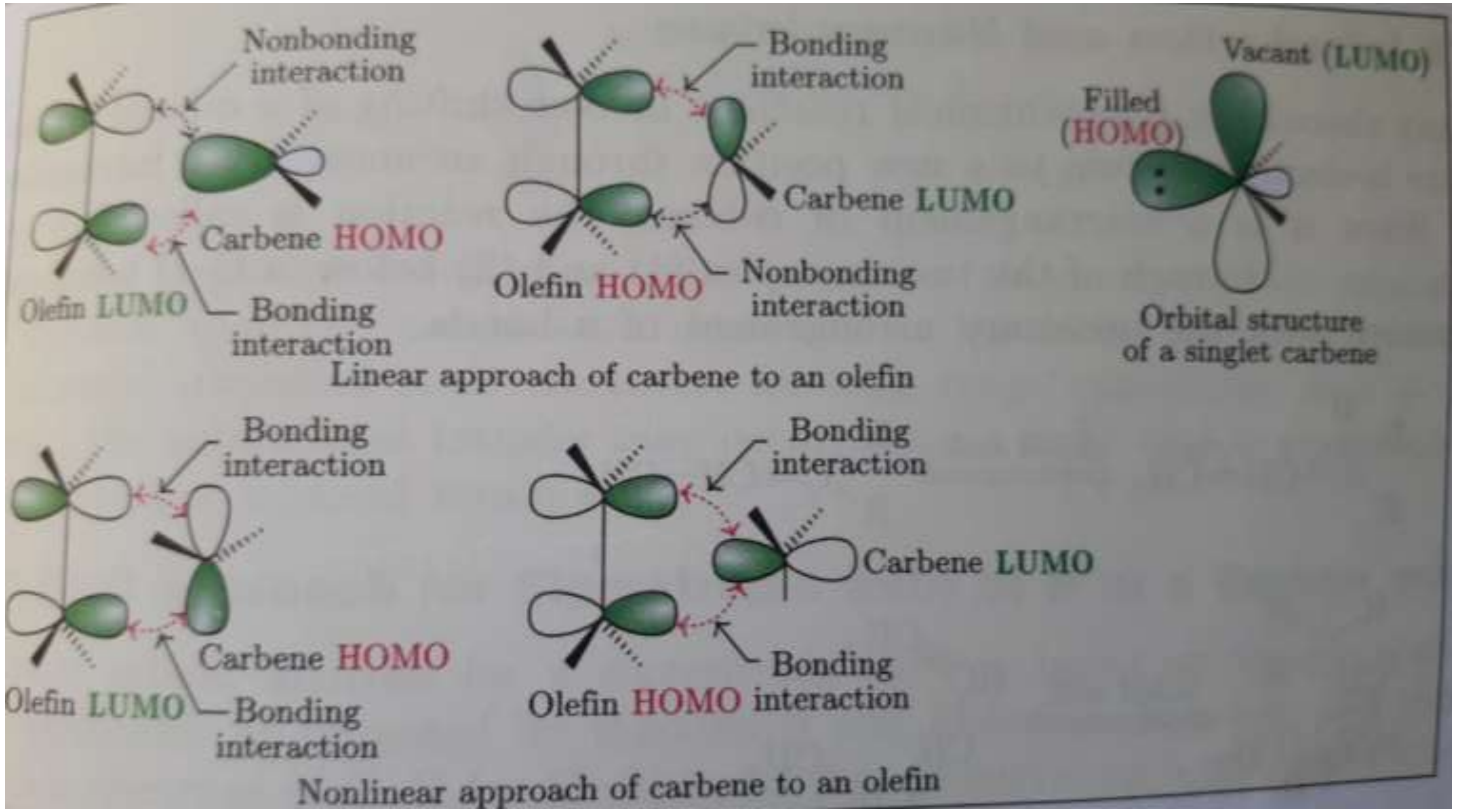
Consider fragment "x" to be a single atom that contributes two electrons to the pericyclic transition state. The approach of "x“ can be either linear or non-linear. The rotation of the π system will be either disrotatory or conrotatory based on the approach of fragment "x"



The HOMO of x points directly at the π system.

The HOMO of x approaches the π system at a skew angle.

Linaer and Nonlinear approach of carbene to an olefin:

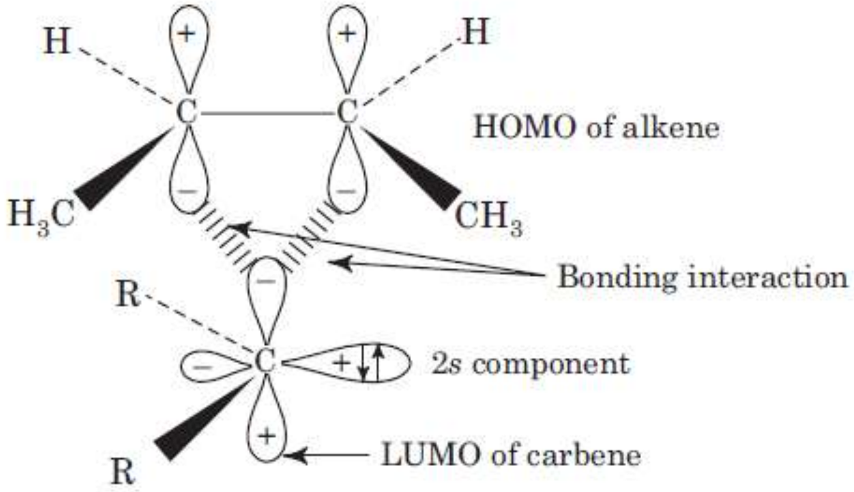


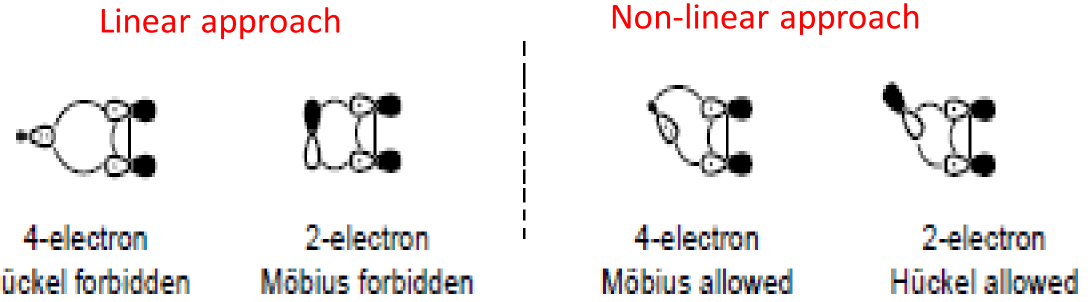
Linear approach of carbene to an olefin

Orbital structure of a singlet carbene

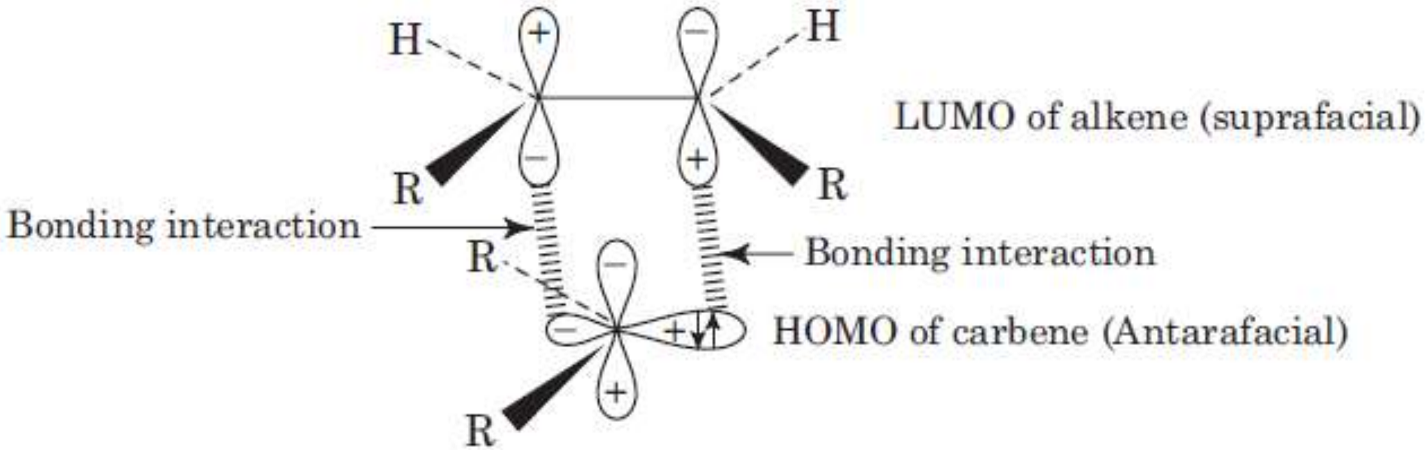
Nonlinear approach of carbene to an olefin

Interaction between HOMO of alkene and LUMO of carbene

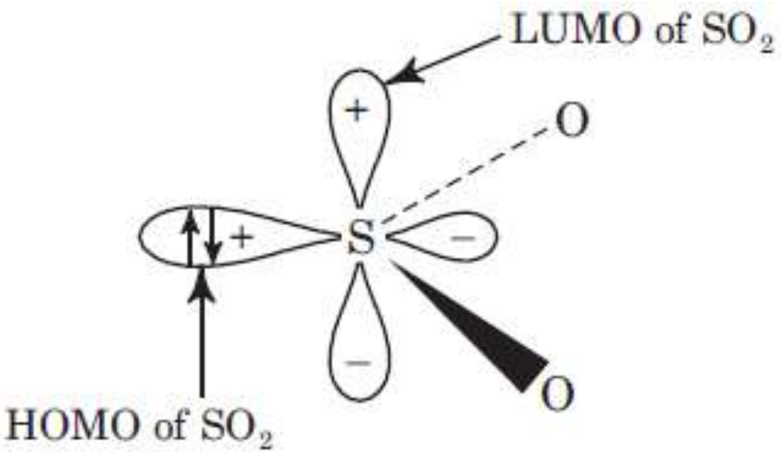


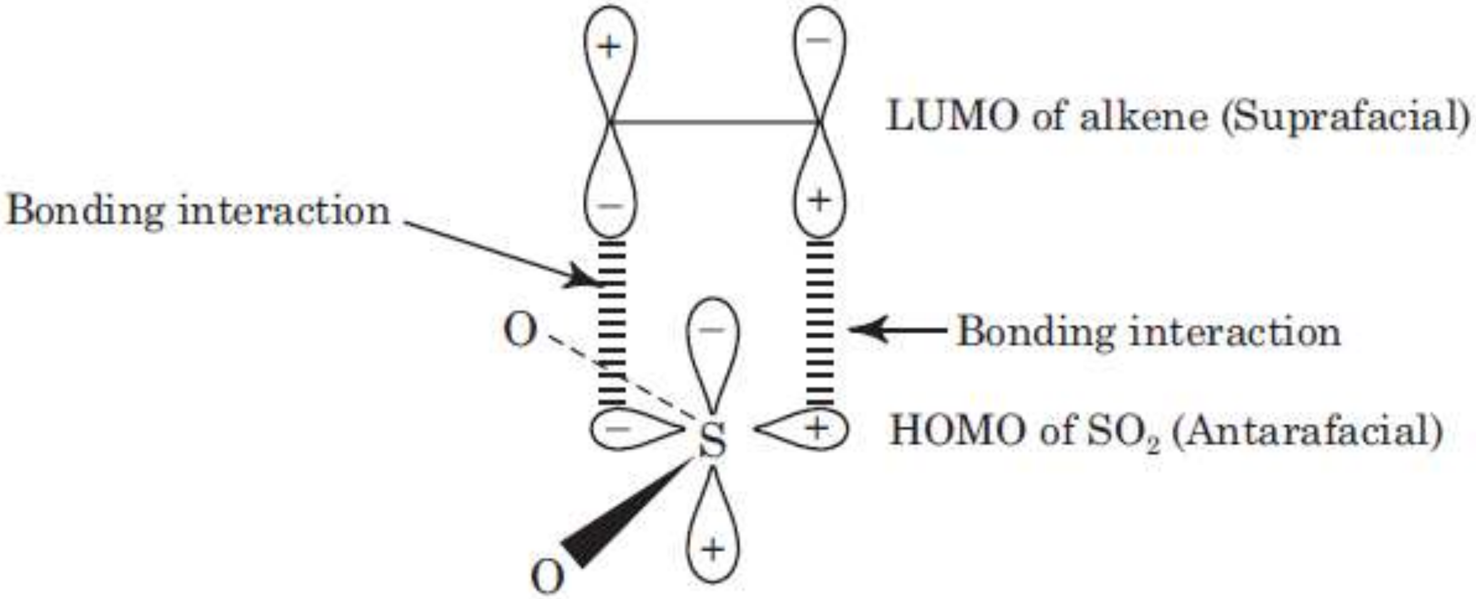


Interaction between LUMO of alkene and HOMO of carbene

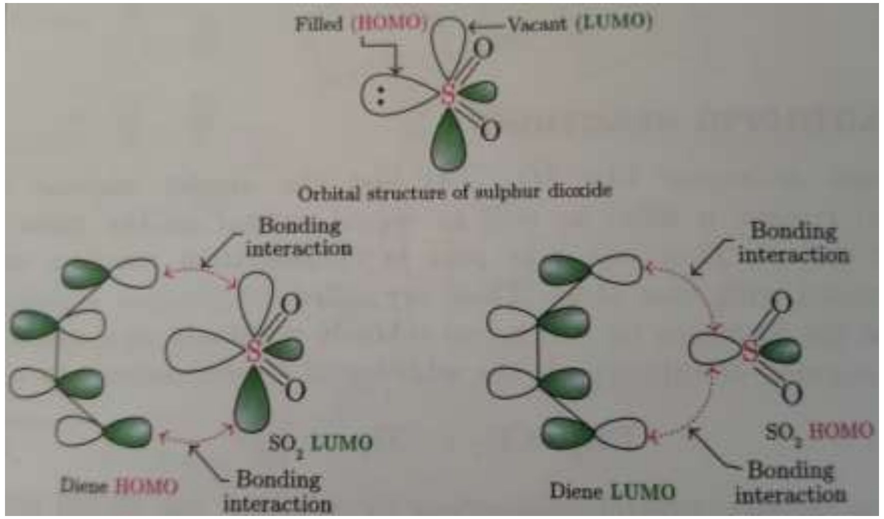


- chelotropic reaction of carbene with alkene is symmetry forbidden if both components interact suprafacially
- Antarafacial reaction of a simple alkene is sterically very unlikely, so that the reaction is likely to involve the :CH2 antarafacially

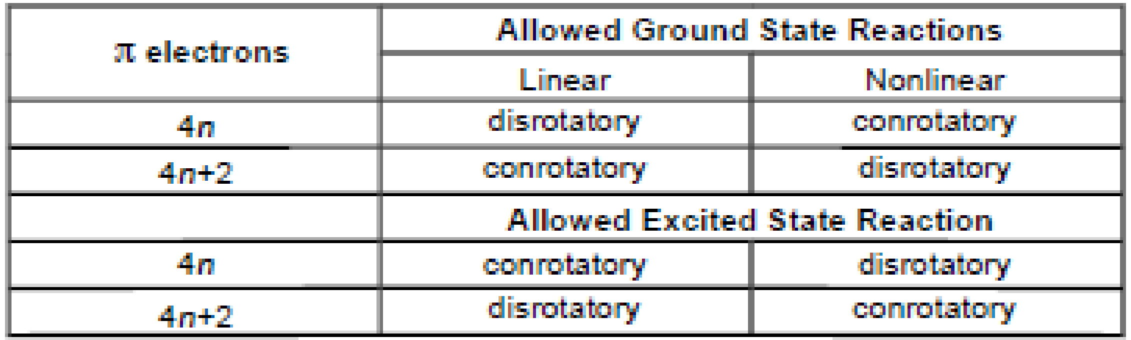




The orbital interaction between SO2 and alkene is as follow:



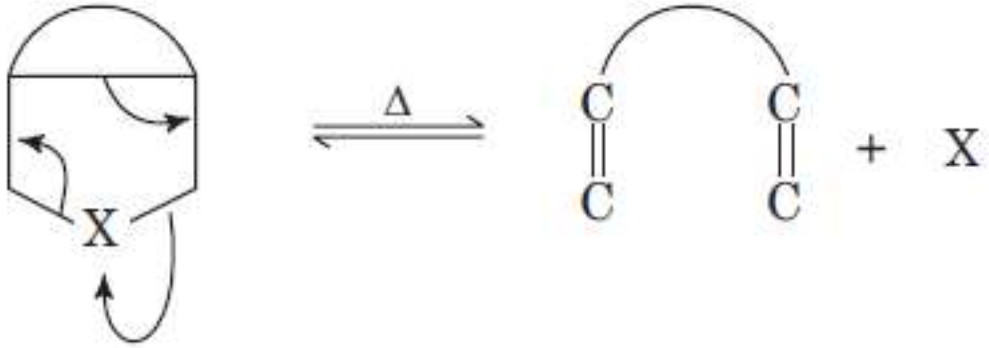
Selection rules for cheletropic reactions



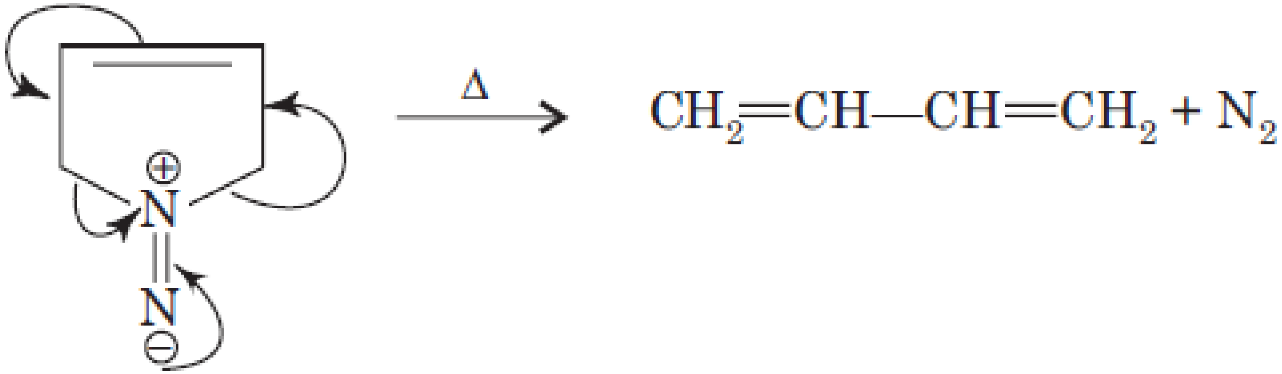
π electrons	Allowed Ground State Reactions	
	Linear	Nonlinear
4*n*	disrotatory	conrotatory
4*n*+2	conrotatory	disrotatory
	Allowed Excited State Reaction	
4*n*	conrotatory	disrotatory
4*n*+2	disrotatory	conrotatory

CHELOTROPIC ELIMINATION

In chelotropic elimination, the atom X is normally bound to other atoms in such a way that elimination will give rise to a stable molecule

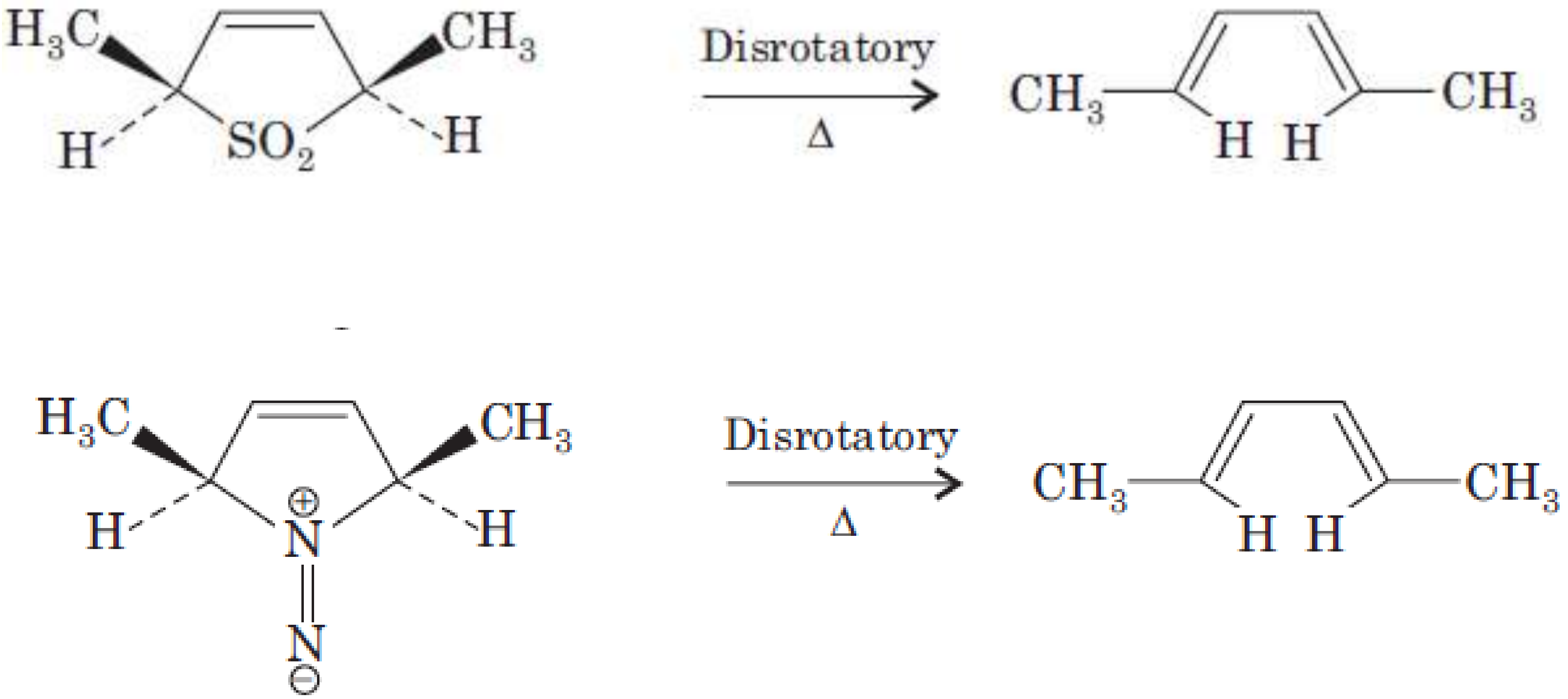


The most common examples involves five membered rings.



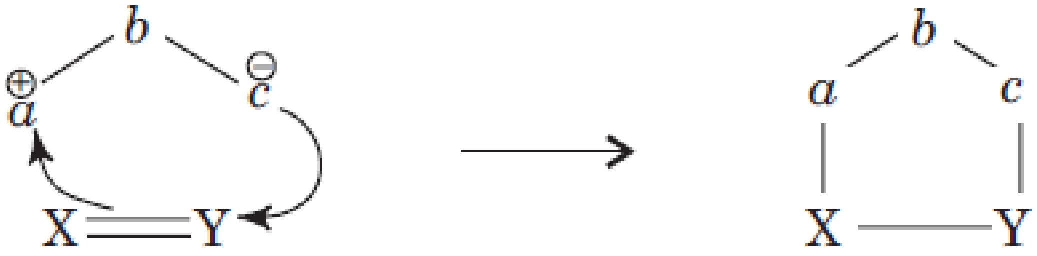
Elimination of diazene in which elimination of nitrogen takes place.

A good example of a concerted chelotropic elimination


H3C
CH3
H
SO2
H
Disrotatory
Δ
CH3
H H
CH3
H3C
CH3
H
N⊕
H
N⊖
Disrotatory
Δ
CH3
H H
CH3

1, 3-DIPOLAR CYCLOADDITIONS

1, 3-dipolar cycloaddition reactions are analogous to the Diels-Alder reaction in that they are concerted [4π + 2π] cycloadditions.
These reactions can be represented as in the given equation:



The species $\overset{\oplus}{a}—b—\overset{\ominus}{c}$ is called the 1, 3-dipolar molecule and X═Y is the dipolarophile.

- The 1, 3-dipolar molecules are isoelectronic with the allyl carbanion and have four electrons in a π (pi) system encompassing the 1, 3-dipole.
- All 1, 3-dipoles contain 4π (pi) electrons in three parallel p-orbitals of a, b and c

Sigmatropic rearrangement:

Sigmatropic rearrangement involves a concerted reorganisation of electrons during which a group attached by a σ (sigma) bond migrates to the terminus of an adjacent π (pi) electron system

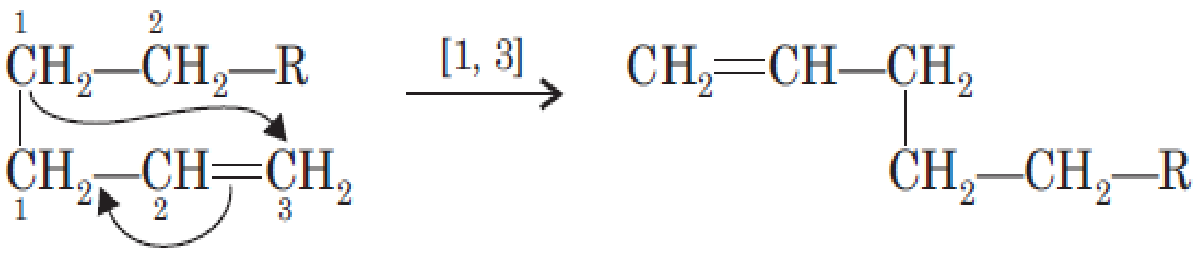
The reactions are called sigmatropic rearrangement because a σ (sigma) bond appears to move from one place to another during the reaction

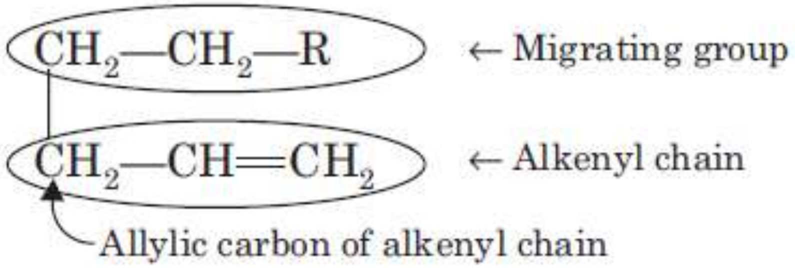
There is a simultaneous shift of the π (pi) electrons

The number of the π (pi) and σ (sigma) bonds remain separately unchanged.

Classification of sigmatropic rearrangement:

Sigmatropic rearrangements are classified by a double numbering system (i, j or m, n)
That refers to the relative positions of the atom or group involved in the migration

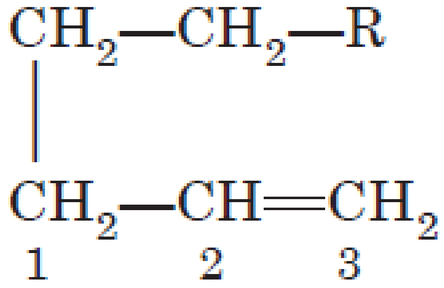




In sigmatropic rearrangement substrate can be divided in two parts: Alkenyl (or polyalkenyl) chain and migrating group. All substrates have at least one allylic carbon in alkenyl chain for sigmatropic rearrangement.

Numbering of Alkenyl Chain

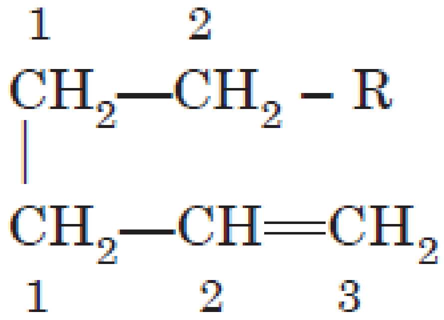
Numbering of alkenyl chain is always started from the allylic carbon and this carbon is numbered-1



$$\begin{array}{l} CH_2-CH_2-R \\ | \\ \underset{1}{CH_2}-\underset{2}{CH}=\underset{3}{CH_2} \end{array}$$

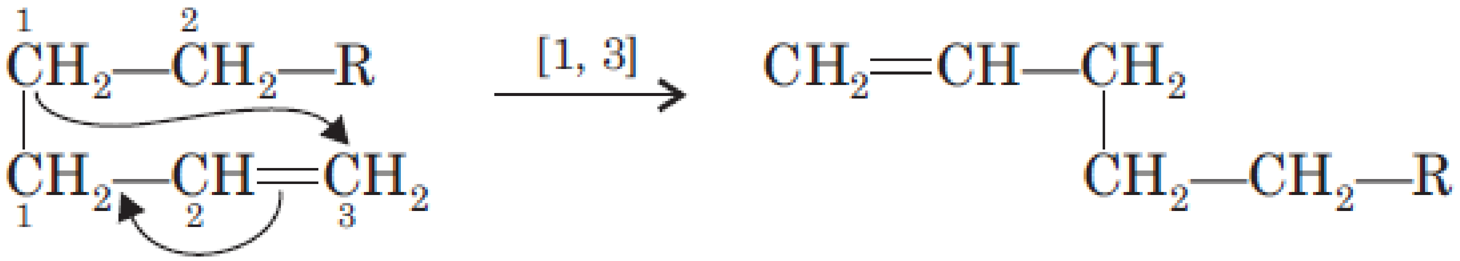
Numbering for Migrating Group

Atom (H, C or heteroatom) of migrating group bonded with allylic carbon by σ (sigma) bond is always given number-1

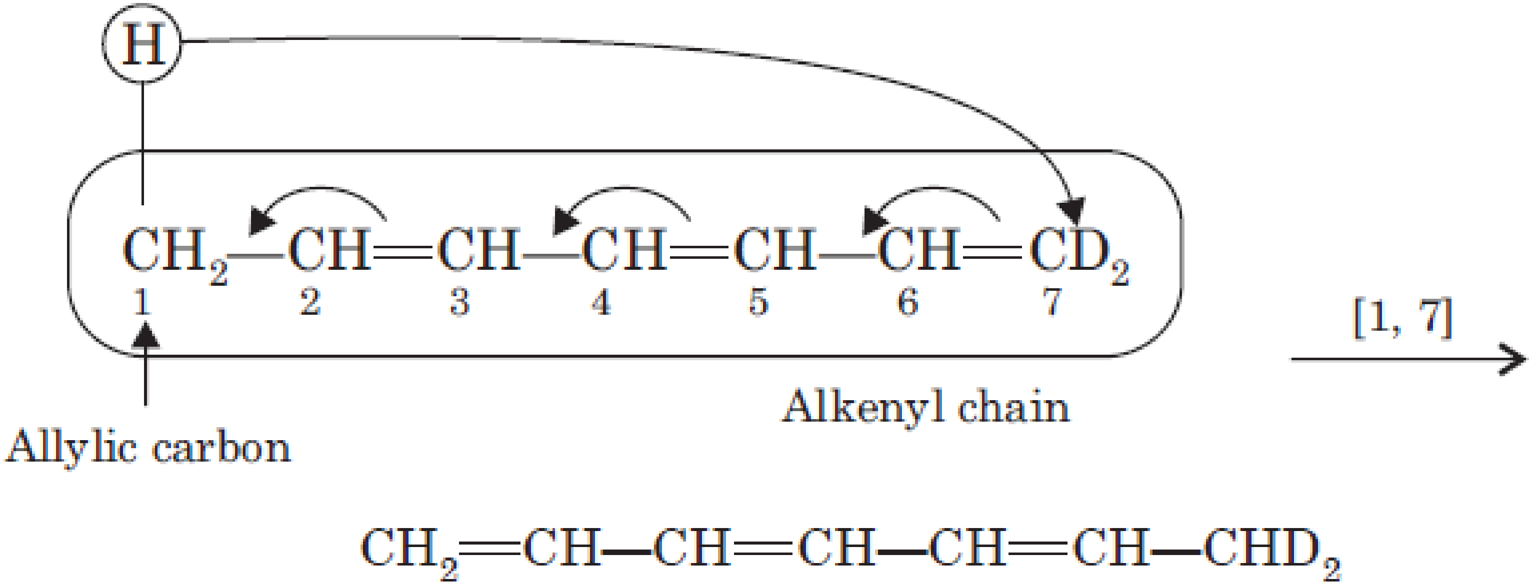


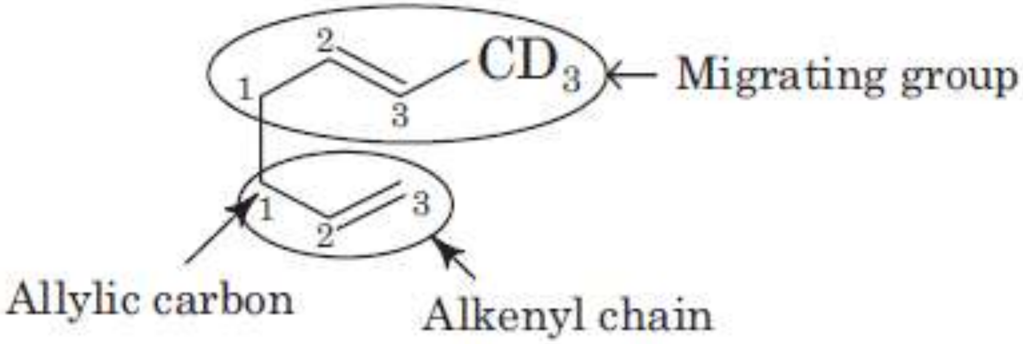
$$\begin{array}{l} \overset{1}{CH_2}-\overset{2}{CH_2}-R \\ | \\ \underset{1}{CH_2}-\underset{2}{CH}=\underset{3}{CH_2} \end{array}$$

In the following example, atom-1 of the migrating group migrates on the atom-3 of the alkenyl chain. Therefore, this rearrangement would be classified as a [1, 3] sigmatropic rearrangement

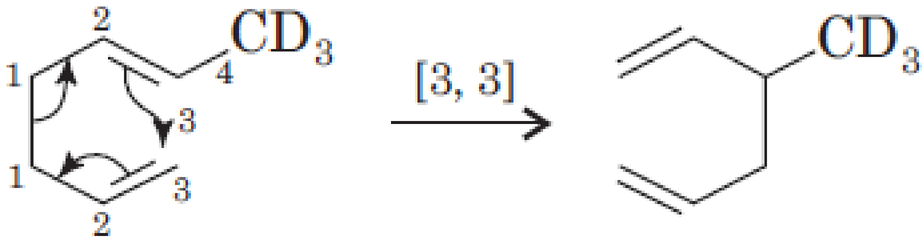


Following is an example of [1, 7] sigmatropic rearrangement





It is not always the first atom of the migrating group that becomes bonded to the alkenyl chain in the rearrangement, will migrate ??????

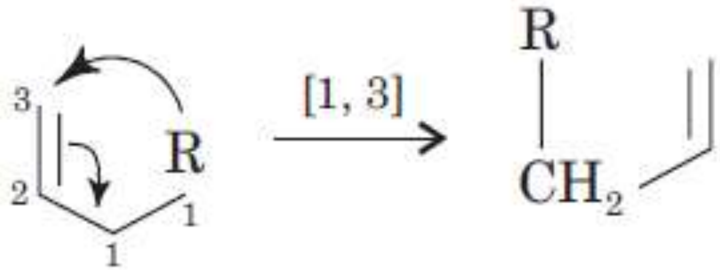


In this rearrangement atom-3 of the migrating group migrates on the atom-3 of the alkenyl chain. Therefore, this rearrangement is an example of [3, 3] sigmatropic rearrangement

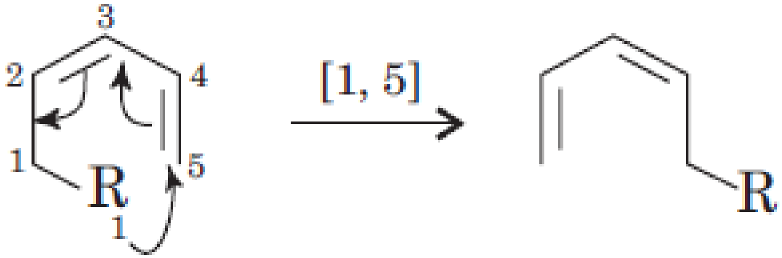
The sigmatropic rearrangements can be divided into **two classes**.

Type 1:

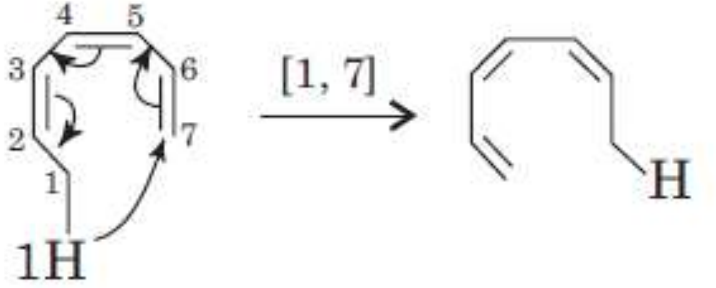
Those where the migrating atom or group is bonded through the same atom in both reactant and product.



R is bonded to carbon in reactant as well as in product



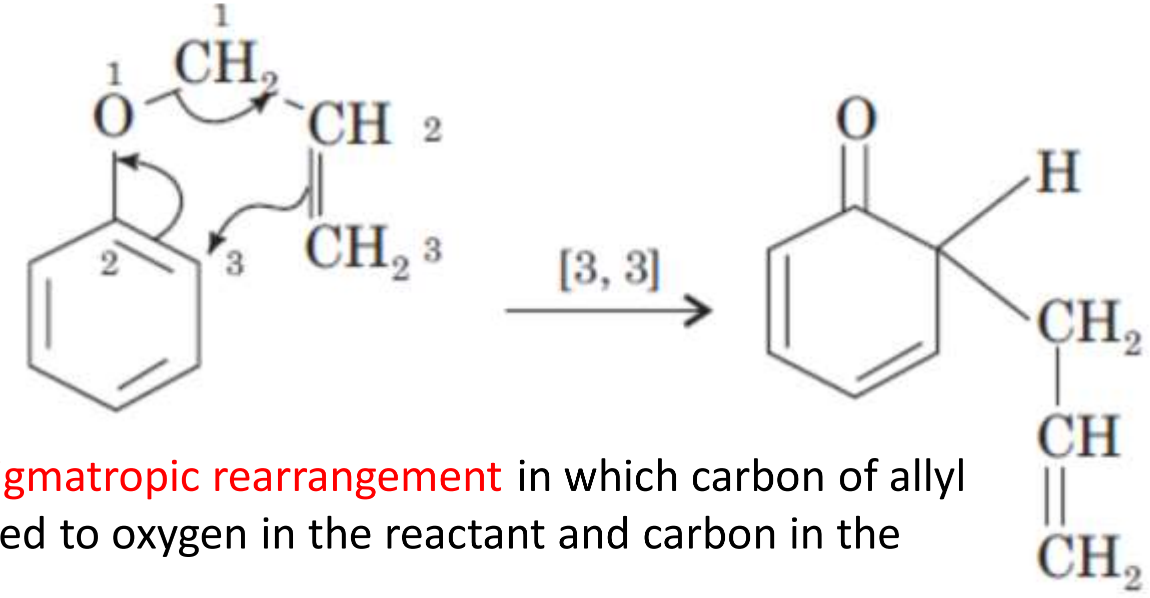
1, 5-shift of alkyl group, R is bonded to carbon in reactant as well as in product



1, 7-shift of hydrogen. H is bonded to carbon in reactant as well as in product

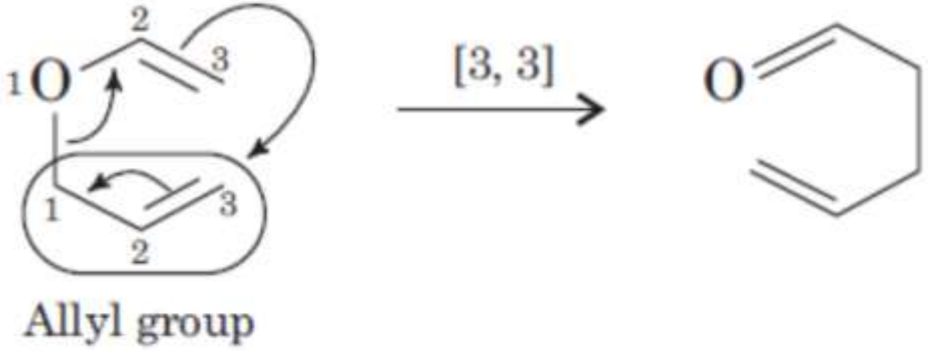
Type 2:

<u>Those where the migrating atom or group is bonded through different atoms in reactant and in product.</u>

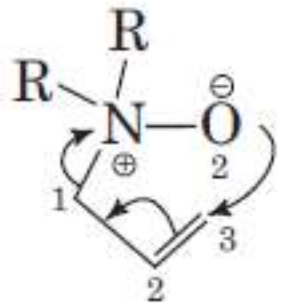


This is [3, 3] sigmatropic rearrangement in which carbon of allyl group is bonded to oxygen in the reactant and carbon in the product.

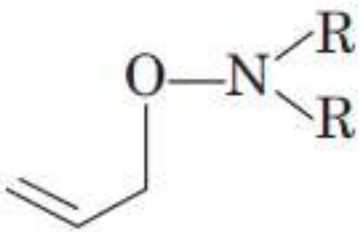
This is [3, 3] sigmatropic rearrangement of an allyl vinyl ether. Migrating group is bonded to the oxygen in the reactant which is bonded to the carbon in the product



[2, 3] Sigmatropic rearrangement of an amine oxide



Allyl group is bonded to nitrogen



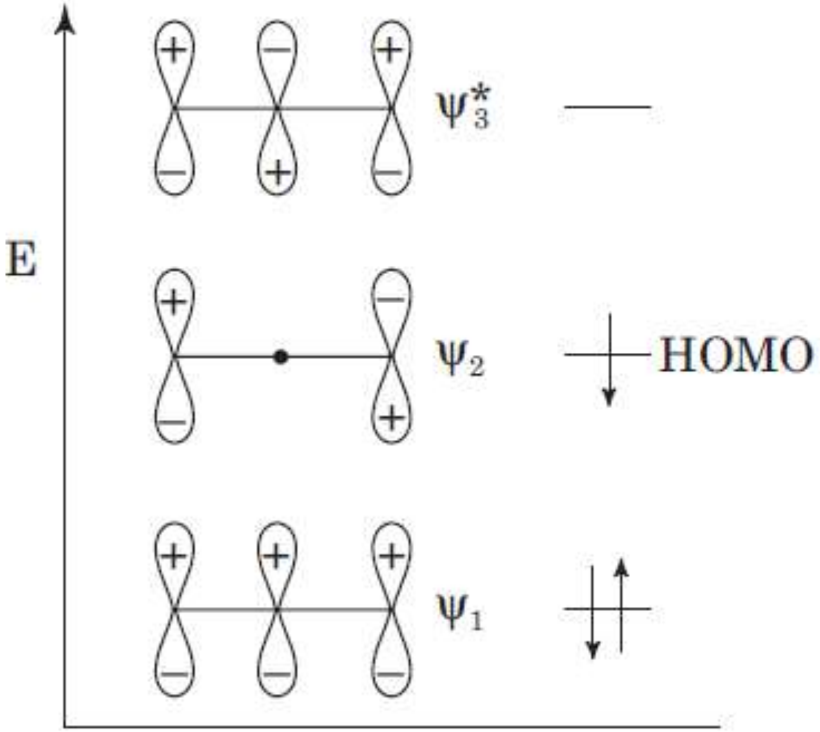
Allyl group is bonded to oxygen

FMO Method

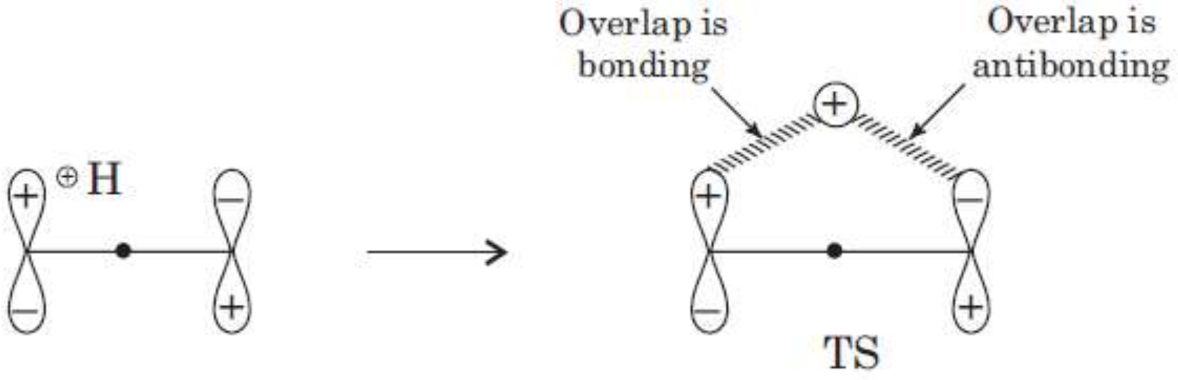
Thermally induced sigmatropic rearrangement which is a [1, 3] shift.

- For the purpose of analysing the orbitals, it is assumed that the σ (sigma) bond connecting the migrating group to its original position undergoes homolytic cleavage to yield two free radicals.
- This is not how the reaction takes place because reaction is concerted.
- This assumption can be explained by the molecular orbitals approach.

The hypothetical cleavage are a hydrogen atom and an allyl free radical, which contains three p-orbitals. The π (pi) molecular orbitals of allyl free radical are shown……….



- In the first case, the migrating group could remain on the same side of the π (pi) orbital system. Such a migration is known as a suprafacial process.
- In the thermal 1, 3 sigmatropic rearrangement a suprafacial migration is geometrically feasible but symmetry forbidden



In the C—H bond the overlapping lobes are of the same sign

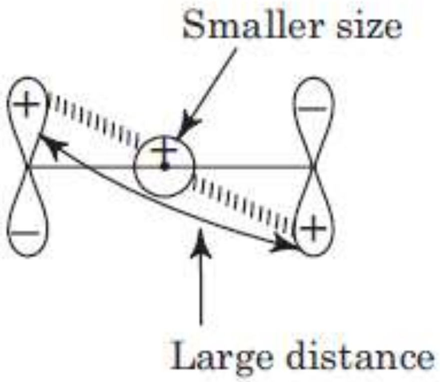
Symmetry forbidden (phase incorrect for overlapping)

Let us consider the second mode of migration for a symmetry allowed [1, 3] sigmatropic shift to occur, the migrating group must shift by an antarafacial process—that is, it must migrate to the opposite face of the orbital system.

Overlap is bonding, symmetry allowed but geometry difficult

While symmetry-allowed a [1, 3] antarafacial sigmatropic rearrangement of hydrogen is not geometrically favorable. Why?

The problem is that the 1s orbital is smallest and cannot effectively span the distance required for an antarafacial migration. In other words, size of 1s orbital of hydrogen is smallest and distance between two lobes of interacting p-orbitals of carbon is maximum hence orbital of 1s cannot interact effectively with p-orbitals at same time in the formation of transition state.



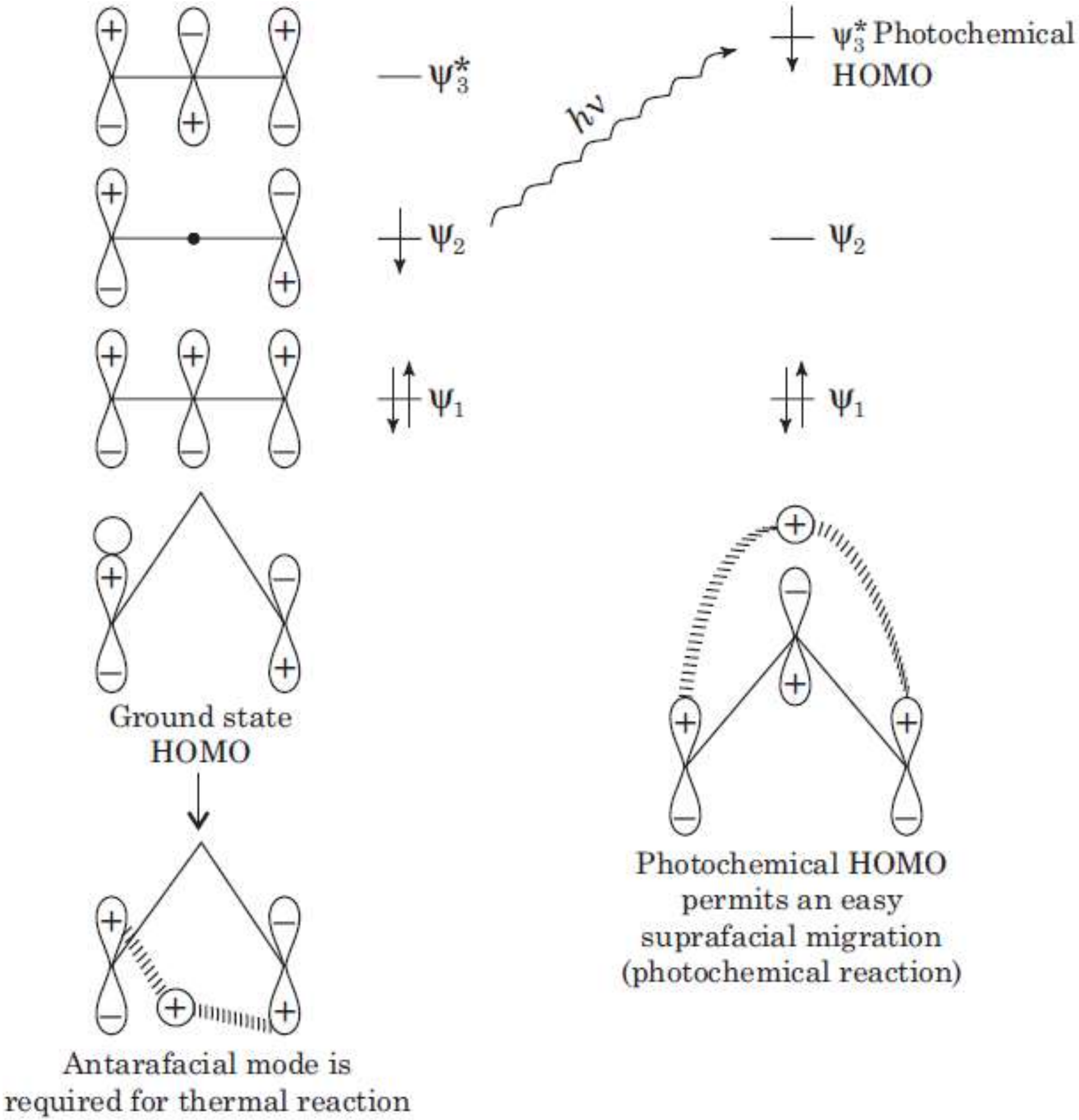
Symmetry allowed but
geometrically difficult

- [1, 3] sigmatropic shifts take place in the presence of UV light but examples are rare.

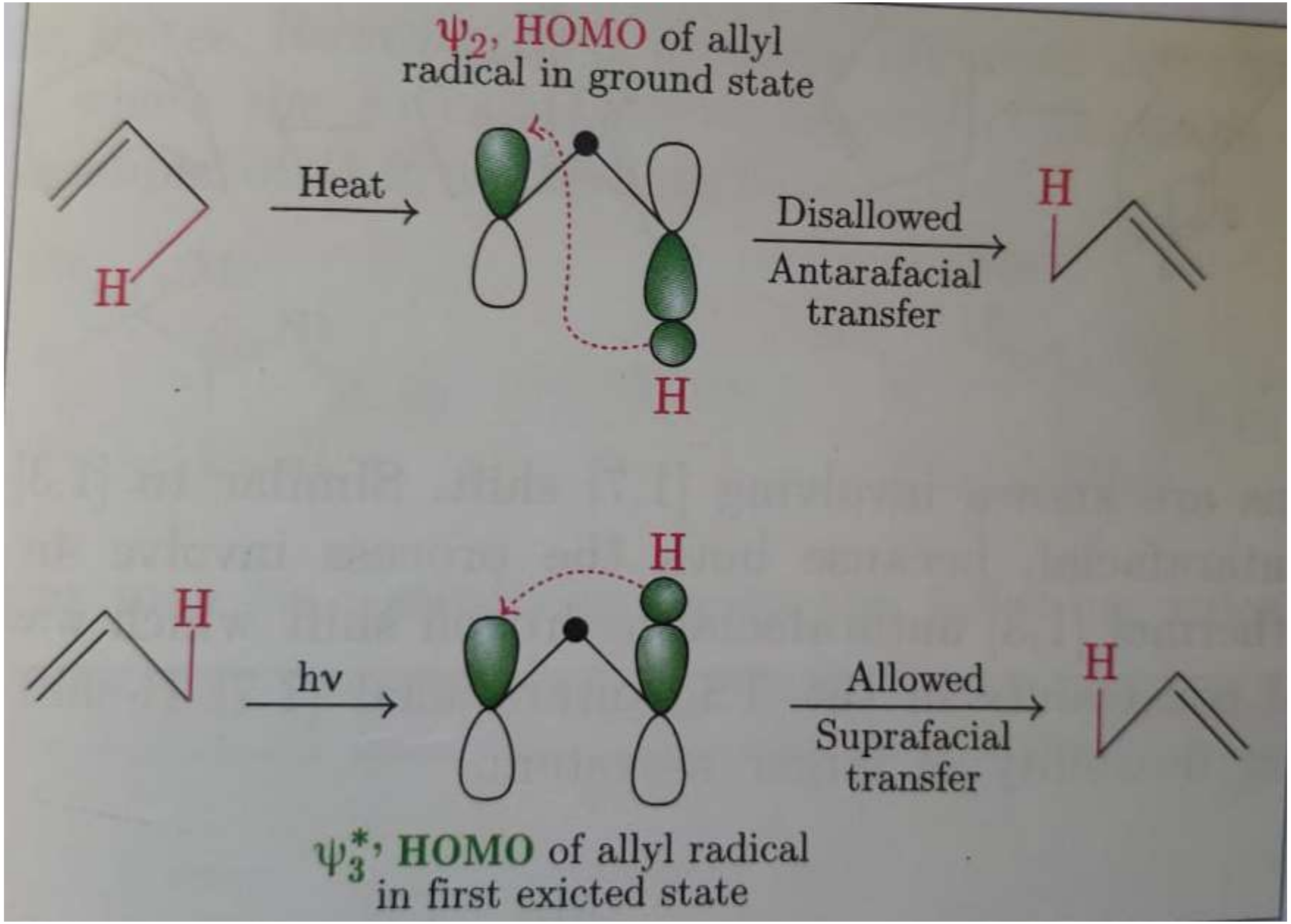
Consider again what happens when a molecule absorbs a photon.

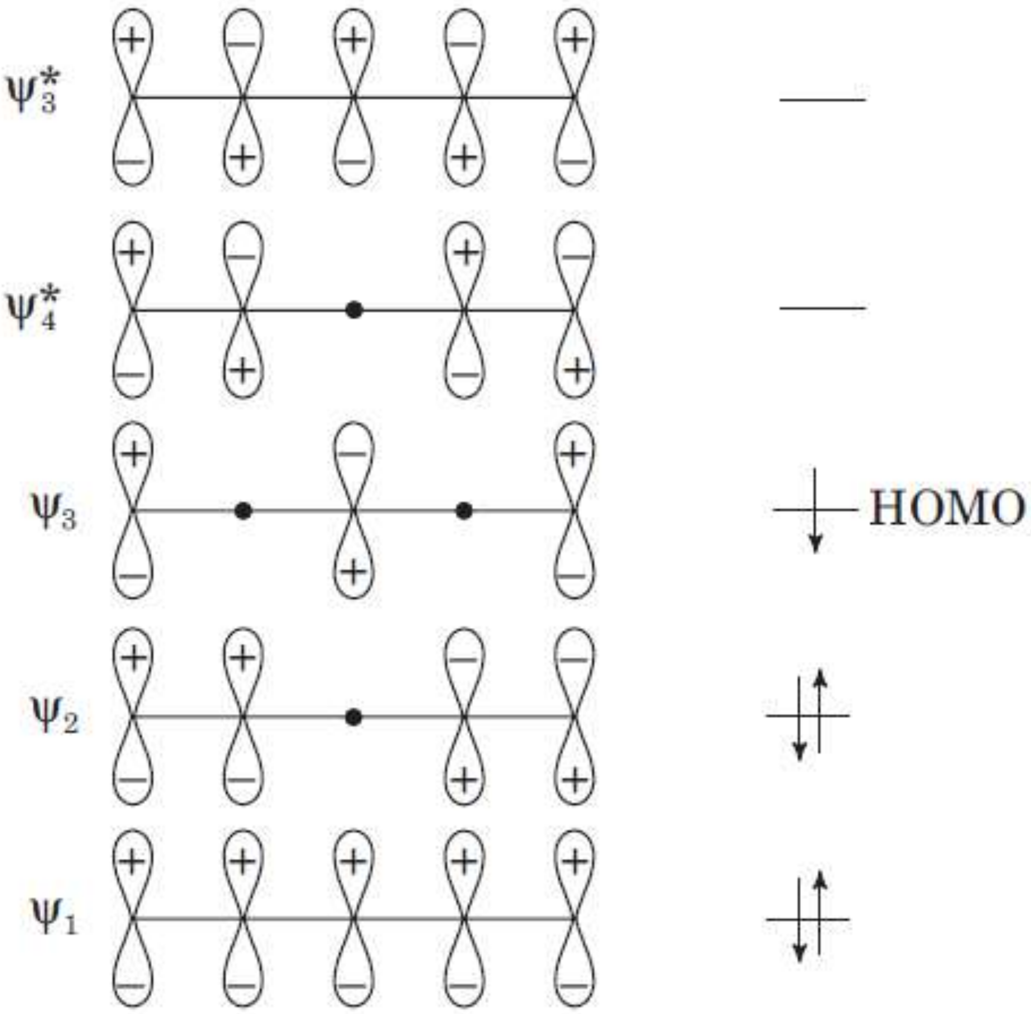
- LUMO of ground state will become HOMO of excited state known as photochemical HOMO

Consider again what happens when a molecule absorbs a photon. LUMO of ground state will become HOMO of excited state known as photochemical HOMO.

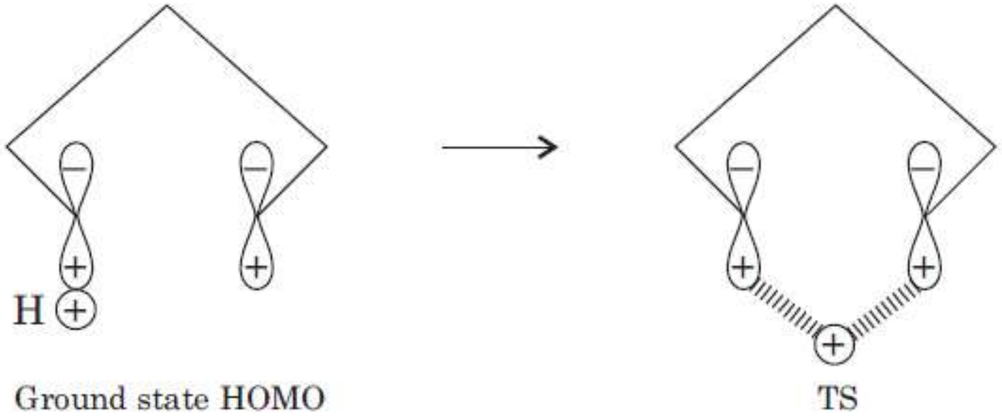


FMO of 1,3 Sigmatropic rearrangement:



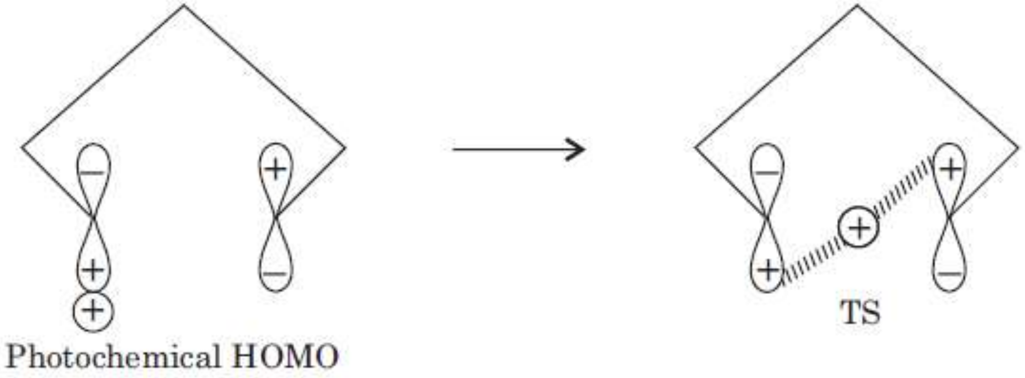


Thermal:



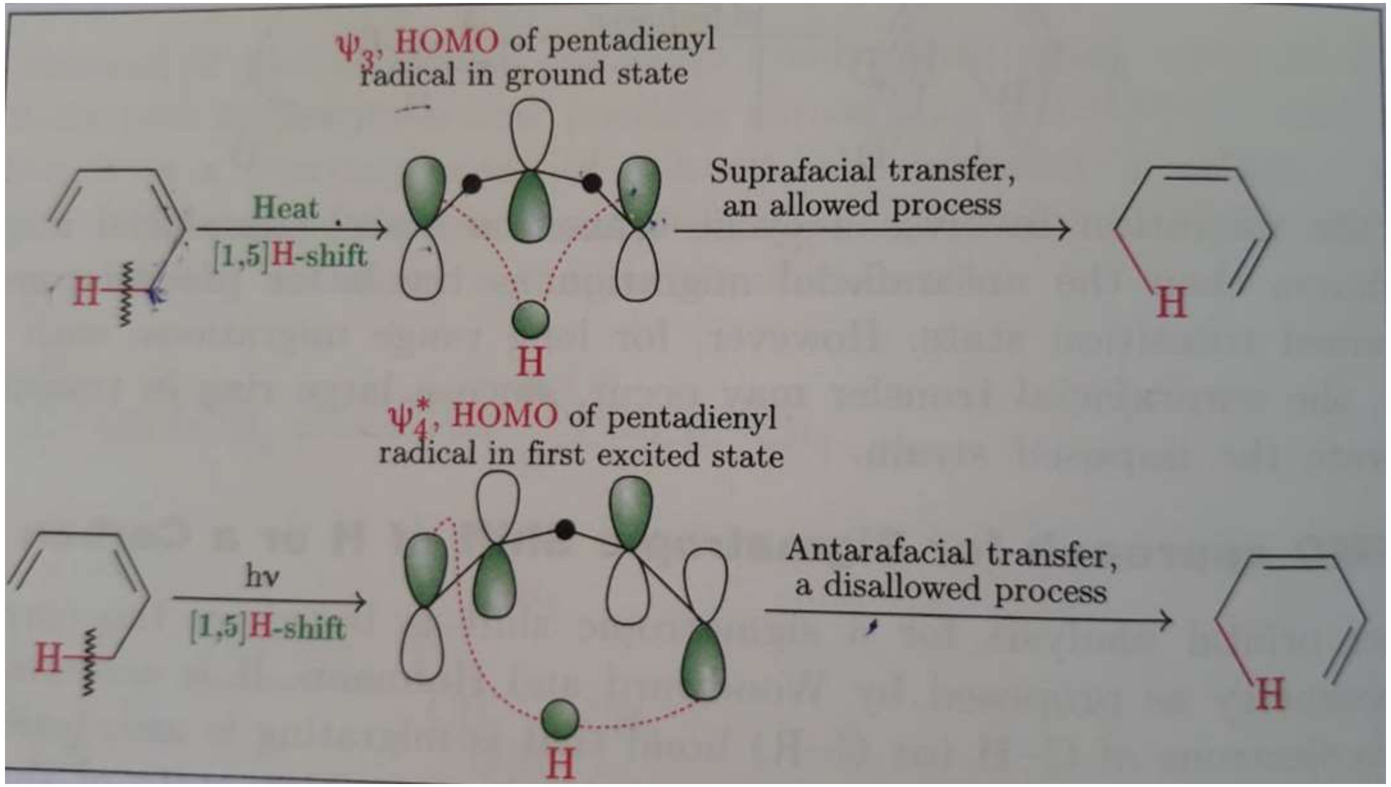
The [1, 5] suprafacial shift is symmetry allowed and geometrically feasible

Photochemical:

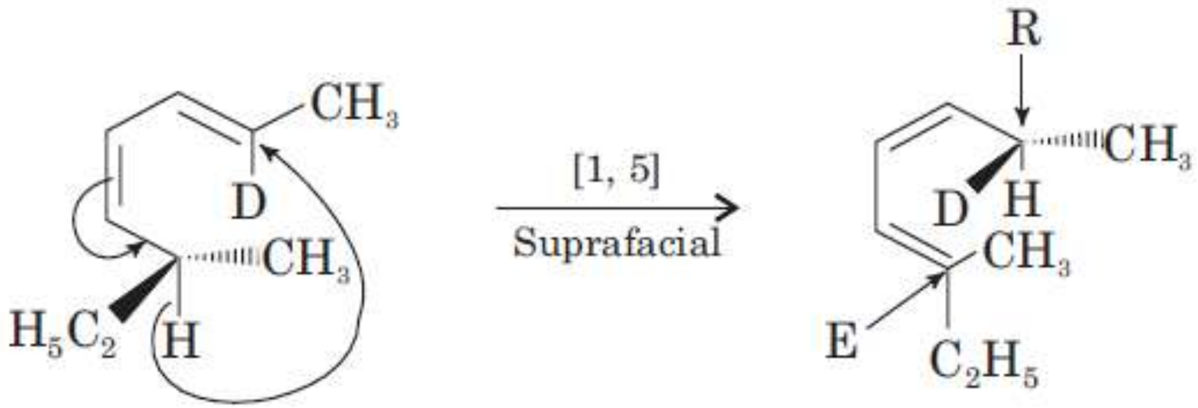


Antarafacial migration, symmetry allowed but geometrically difficult

1,5-sigmatropic rearrangement:

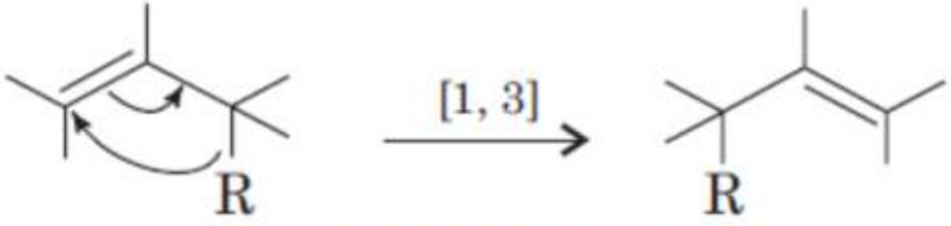


Stereochemistry of [1, 5] sigmatropic Rearrangement

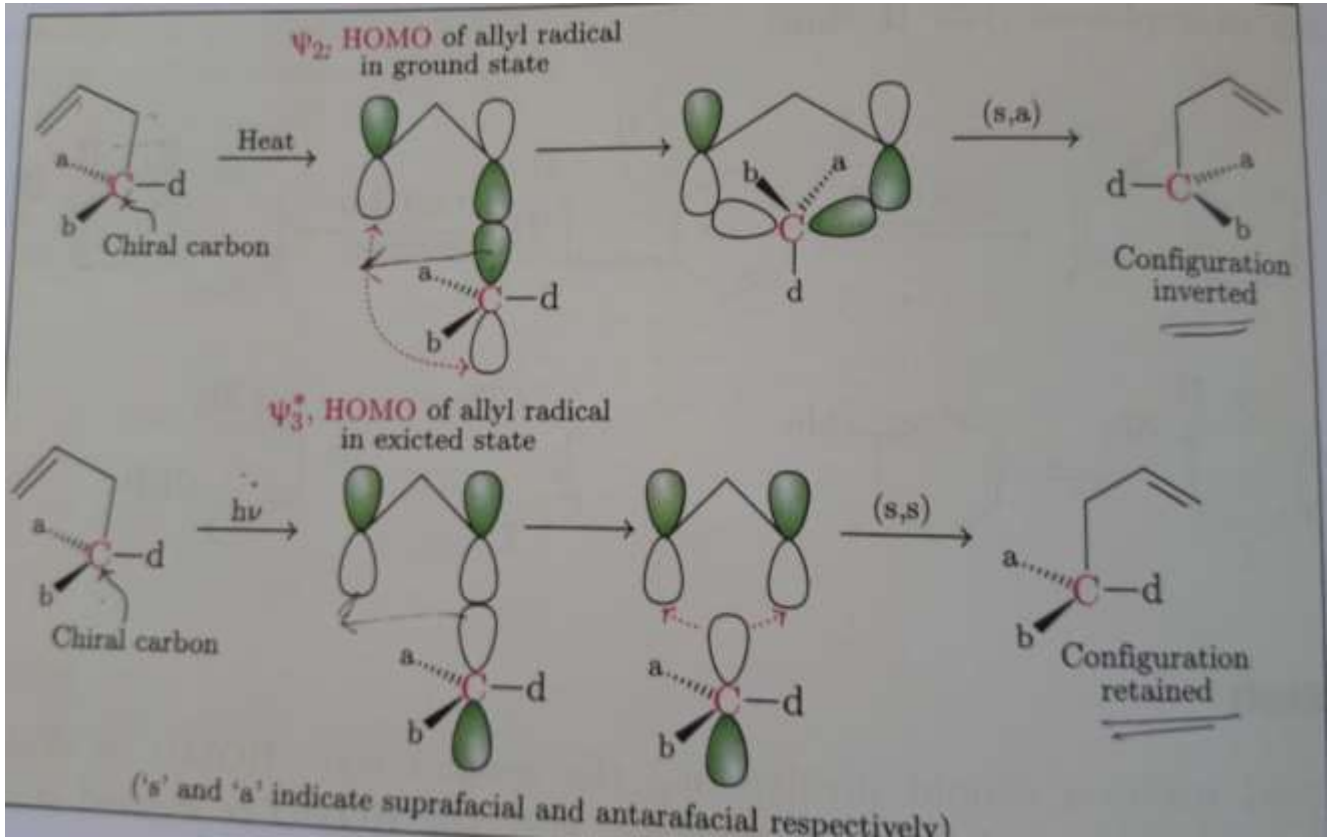


If migration is suprafacial then product has R-configuration at C-5 and E-configuration at C-1.

Sigmatropic shifts of Alkyl group:



1, 3-Alkyl shift



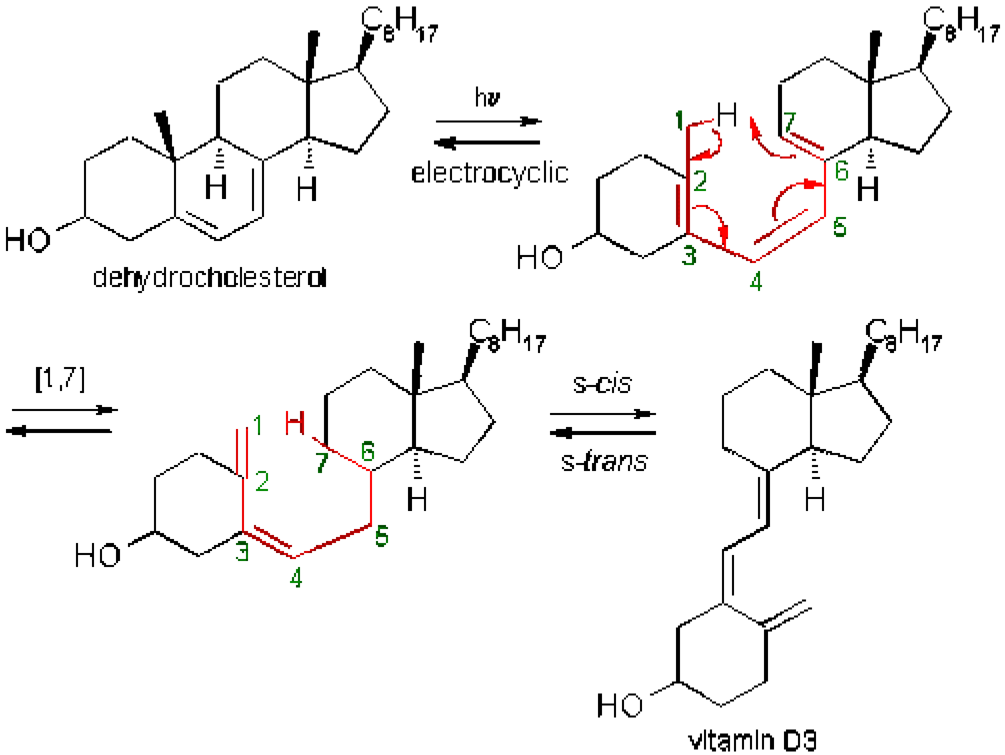
('s' and 'a' indicate suprafacial and antarafacial respectively)

Table 4.1 Selection rule for [1 + n] in which migrating group is hydrogen

$m+n$	*Thermal allowed photochemical forbidden*	*h*ν *allowed* Δ *forbidden*
$4q$	antara	supra
$4q+2$	supra	antara

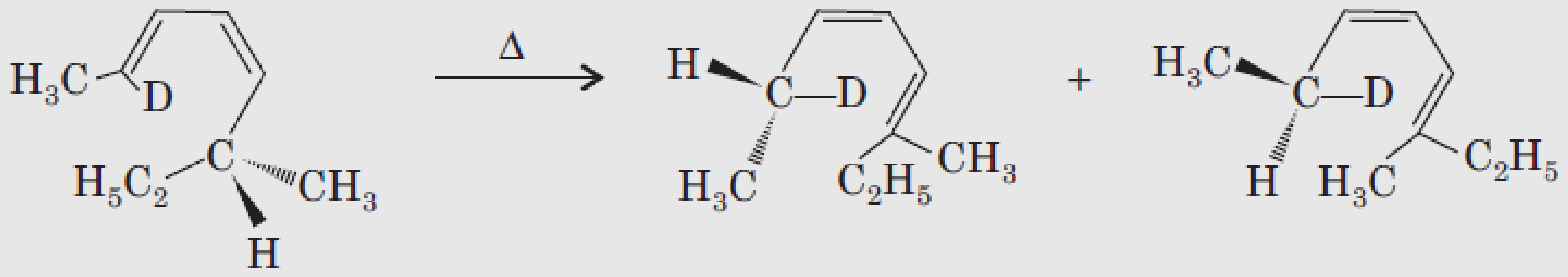
Application:

Vitamin D3 synthesis in presence of Sunlight (1,7 sigmatropic rearrangement)



Work out the following…..

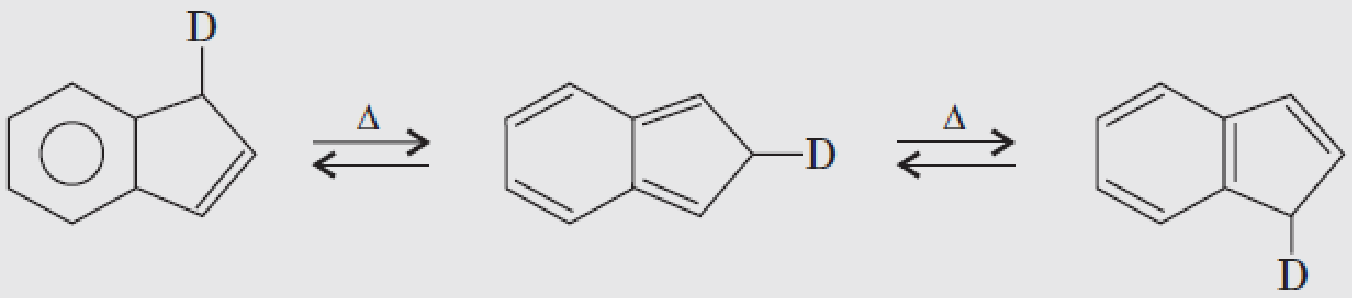
1. Explain the following observations:



2. What do you understand from the order [*m*, *n*] of a sigmatropic rearrangement? Explain giving examples.

3. [1, 3] Sigmatropic shift of hydrogen is thermally forbidden but photochemically allowed. Explain.

4. On heating 3-deuterioindene scrambling of the label to all the three positions in the five membered ring takes place. Explain.



[**Hint:** This scrambling is a result of a series of [1, 5] shifts].