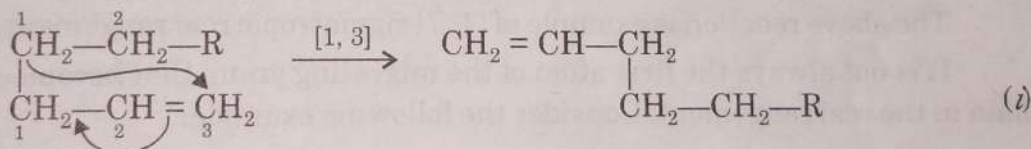# Sigmatropic Rearrangement

4.1 INTRODUCTION AND CLASSIFICATION

Sigmatropic rearrangements are another class of concerted pericyclic reactions governed by orbital symmetry. This rearrangement involves a concerted reorganisation of electrons during which a group attached by a *sigma* bond migrates to the terminus of an adjacent *pi* electron system. The reactions are called sigmatropic rearrangement because a *sigma* bond appears to move from one place to another during the reaction. There is a simultaneous shift of the *pi* electrons. The number of the *pi* and *sigma* bonds remains separately unchanged.
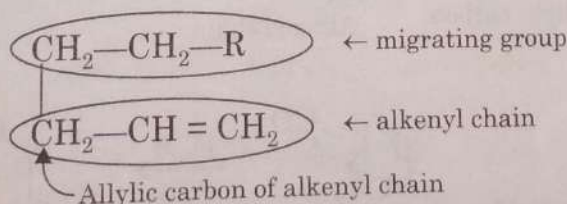
Classification of Sigmatropic Rearrangements

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. This method of classification is different from those for cycloaddition or electrocyclic reactions which are classified by the number of *pi* electrons involved in the cyclic transition state.

The method used in classifying sigmatropic rearrangement is best explained by the following examples.

$$\overset{1}{C}H_2 - \overset{2}{C}H_2 - R \quad \overset{[1,3]}{\longrightarrow} \quad CH_2 = CH - CH_2$$
$$\underset{1}{C}H_2 - \underset{2}{C}H = \underset{3}{C}H_2 \qquad\qquad CH_2 - CH_2 - R \qquad (i)$$

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.
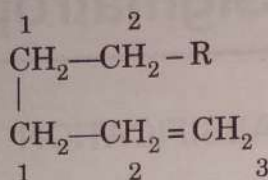
$$CH_2 - CH_2 - R \qquad \leftarrow \text{migrating group}$$
$$CH_2 - CH = CH_2 \qquad \leftarrow \text{alkenyl chain}$$
$$\quad\text{Allylic carbon of alkenyl chain}$$

Numbering of Alkenyl Chain
Numbering of alkenyl chain is always started from the allylic carbon and this carbon is numbered – 1

97

$$CH_2—CH_2—R$$
$$|$$
$$CH_2—CH = CH_2$$
$$\ \ 1 \qquad\ 2 \qquad\quad 3$$
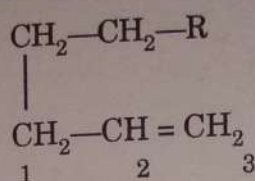
Numbering for Migrating Group

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

$$\ \ 1 \qquad\quad 2$$
$$CH_2—CH_2 - R$$
$$|$$
$$CH_2—CH_2 = CH_2$$
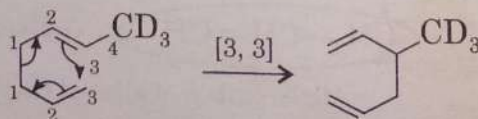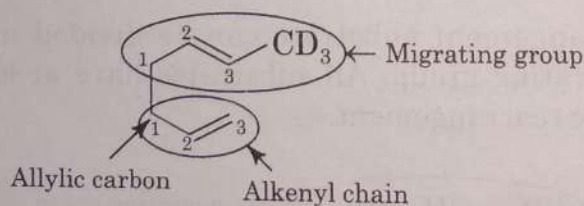$$\ \ 1 \qquad\ 2 \qquad\quad 3$$

Name of the Rearrangement

In the example (*i*) 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. In 1, 3 [(*i.e. i, j*) *i* = 1 and *j* = 3] *i* indicates position of atom in the migrating group and *j* indicates position of atom in the alkenyl chain.

$$CH_2 = CH—CH = CH—CH = CH—CHD_2 \qquad\qquad (ii)$$
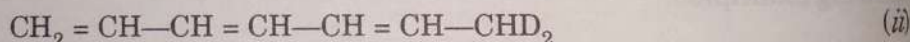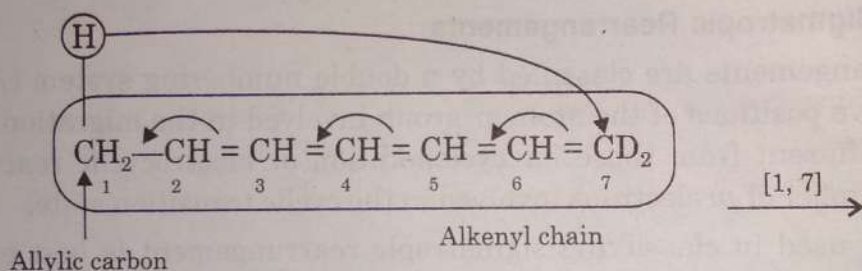
The above reaction is example of [1, 7] sigmatropic rearrangement.

It is not always the first atom of the migrating group that becomes bonded to the alkenyl chain in the rearrangement. Consider the following example:


(*iii*)

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.

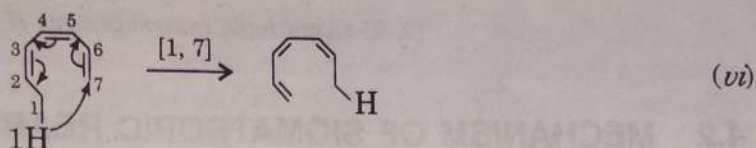The sigmatropic rearrangements can be divided into *two classes*.

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

(*iv*)

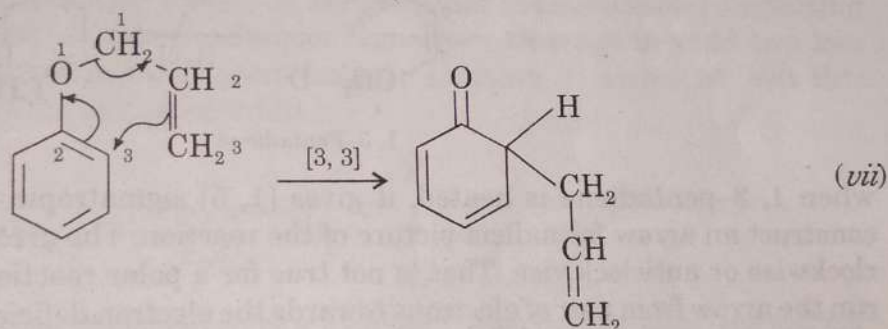R is bonded to carbon in reactant as well as in product

(*v*)
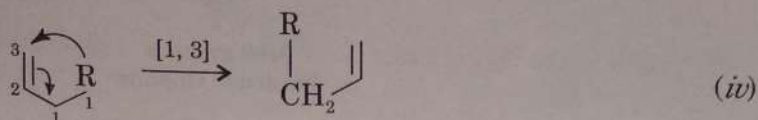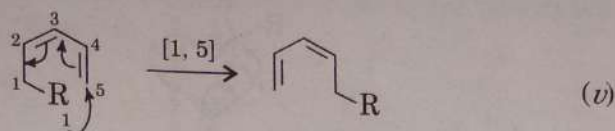
1, 5—shift of alkyl group, R is bonded to carbon in reactant as well as in product
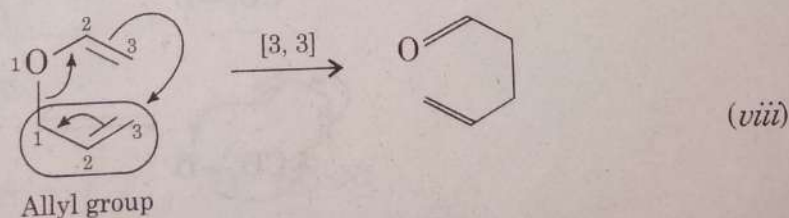

(*vi*)

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

2. Those where the migrating atom or group is bonded through different atoms in reactant and in product.

(*vii*)

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

(*viii*)

Allyl group

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.

Allyl group is
bonded to sulphur

Allyl group is
bonded to oxygen

(ix)
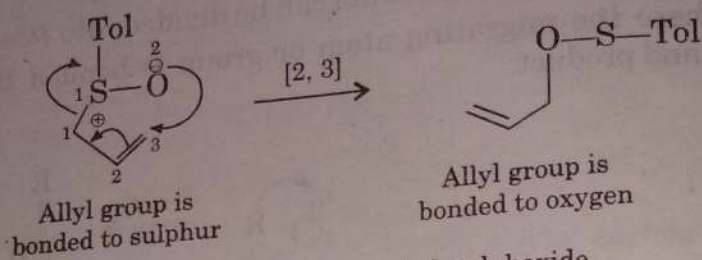
[2, 3] sigmatropic rearrangement of an allyl sulphoxide

Allyl group is
bonded to nitrogen

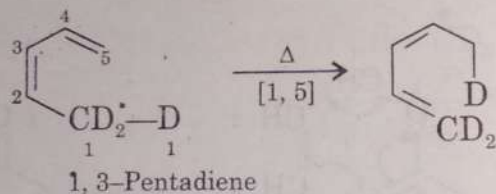Allyl group is
bonded to oxygen

(x)
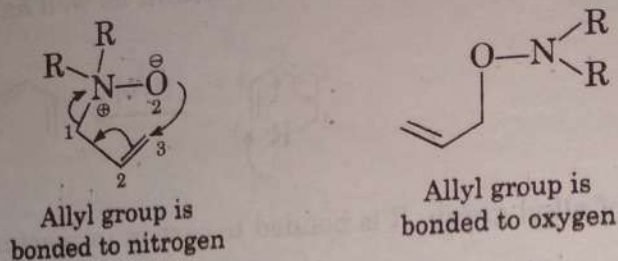
[2, 3]-sigmatropic rearrangement of an amine oxide

4.2 MECHANISM OF SIGMATROPIC REARRANGEMENT

FMO Method

Consider the following reaction

1, 3–Pentadiene

when 1, 3–pentadiene is heated, it gives [1, 5] sigmatropic rearrangement. It is simple to construct an arrow formalism picture of the reaction. The arrow could run in either direction, clockwise or anticlockwise. That is not true for a polar reaction in which the convention is to run the arrow from pair of electrons towards the electron deficient.
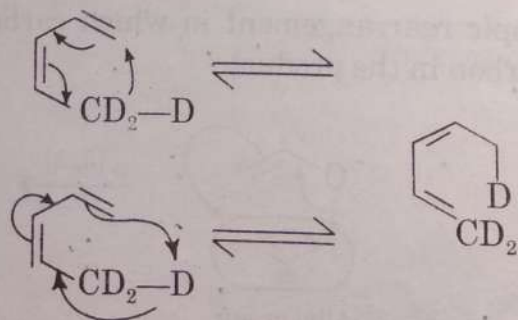

An arrow formalism description of the [1, 5] shift of deuterium in 1, 3-pentadiene.

In the given example deuterium of sp^3 hybrid carbon migrates on to the sp^2 hybrid carbon (carbon–5). The given compound has also carbon–3 as sp^2 hybrid carbon. Thus this compound can also give [1, 3] sigmatropic rearrangement on heating, but [1, 3] shift is not observed.

[1, 3] ↛

CD$_2$—D   CD$_2$
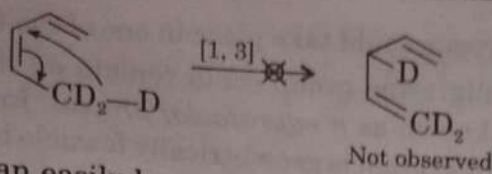
Not observed

An arrow formalism can easily be written and it might be reasonably argued that the [1, 3] shift requiring a shorter path than the [1, 5] shift, should be easier than why [1, 3] shifts not observed on heating?
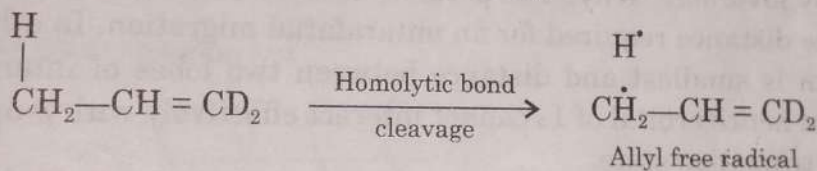
A second strange aspect of this reaction comes from photochemical experiments. When 1, 3–pentadienes are irradiated the product of the reaction include the molecules formed through [1, 3] shift but not those of [1, 5] shifts.

$\xrightarrow{h\nu}$

CD$_2$—D

Product of a [1, 3] shift
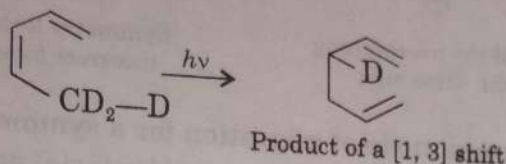
So any mechanism proposed must include an explanation of why thermal shifts are [1, 5] whereas photochemically induced shifts are [1, 3]. We can use the frontier orbital approach to analyse these reactions and see why this is so. Let us first consider the following thermally induced sigmatropic rearrangement which is a [1, 3] shift.

$$\overset{\overset{\textstyle H}{\textstyle |}}{CH_2}—CH = CD_2 \quad \xrightarrow{\Delta} \quad CH_2 = CH—CHD_2$$
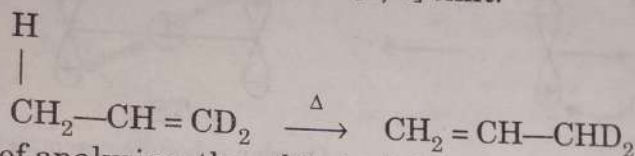
For the purpose of analysing the orbitals, it is assumed that the *sigma* bond connecting the migrating group to its original position undergoes homolytic cleavage to yield two free radicals. This is not how the reaction takes place because reaction is concerted. But this assumption does allow analysis of the molecular orbitals.

$$\overset{\overset{\textstyle H}{\textstyle |}}{CH_2}—CH = CD_2 \quad \xrightarrow[\text{cleavage}]{\text{Homolytic bond}} \quad \overset{\textstyle H^{\bullet}}{} \quad \overset{\bullet}{C}H_2—CH = CD_2$$

Allyl free radical

The products of the hypothetical cleavage are a hydrogen atom and an allyl free radical, which contains three *p*-orbitals. The *pi* molecular orbitals of allyl free radical are shown in Fig. 4.1.
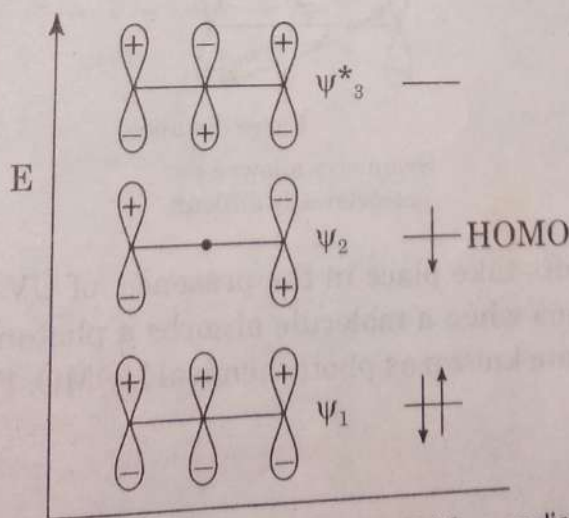

Fig. 4.1 Molecular orbitals of allyl free radical

The actual shift of hydrogen could take place in one of the two directions.

In the first case, the migrating group could remain on the same side of the *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)
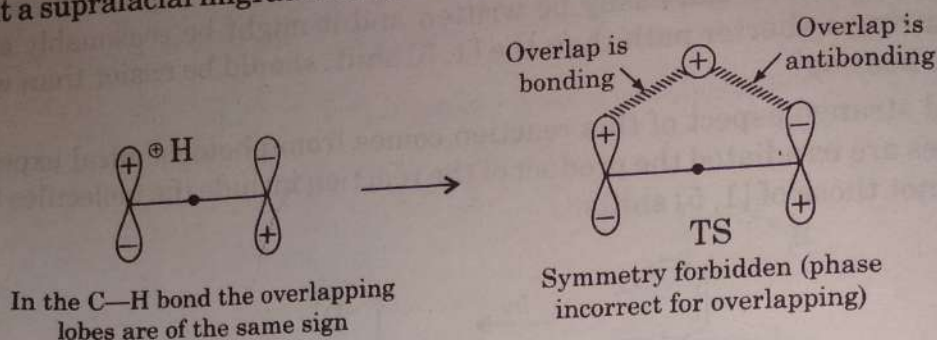
Let us consider the second mode of migration for a symmetry allowed [1, 3] sigmatropic shift to occur, the migrating group must shift by an antarafacial process—that is it must migrate to the *opposite face* of the orbital system.

Overlap is bonding, symmetry allowed but geometry difficult
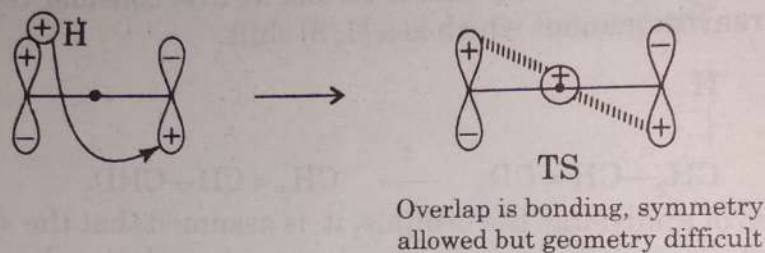
While symmetry-allowed a [1, 3] antarafacial sigmatropic rearrangement of hydrogen is not geometrically favorable. Why? The problem is that the 1s orbital is smallest and cannot effectively span the distance required for an antarafatial migration. In other words, size of 1s orbital of hydrogen is smallest 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.

Smaller size

Large distance

Symmetry allowed but geometrically difficult
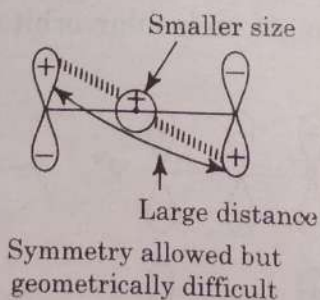
[1, 3] sigmatropic shifts take place in the presence of UV light but examples are rare. Consider again what happens when a molecule absorbs a photon. LUMO of ground state will become HOMO of excited state known as photochemical HOMO. Fig. 4.2.
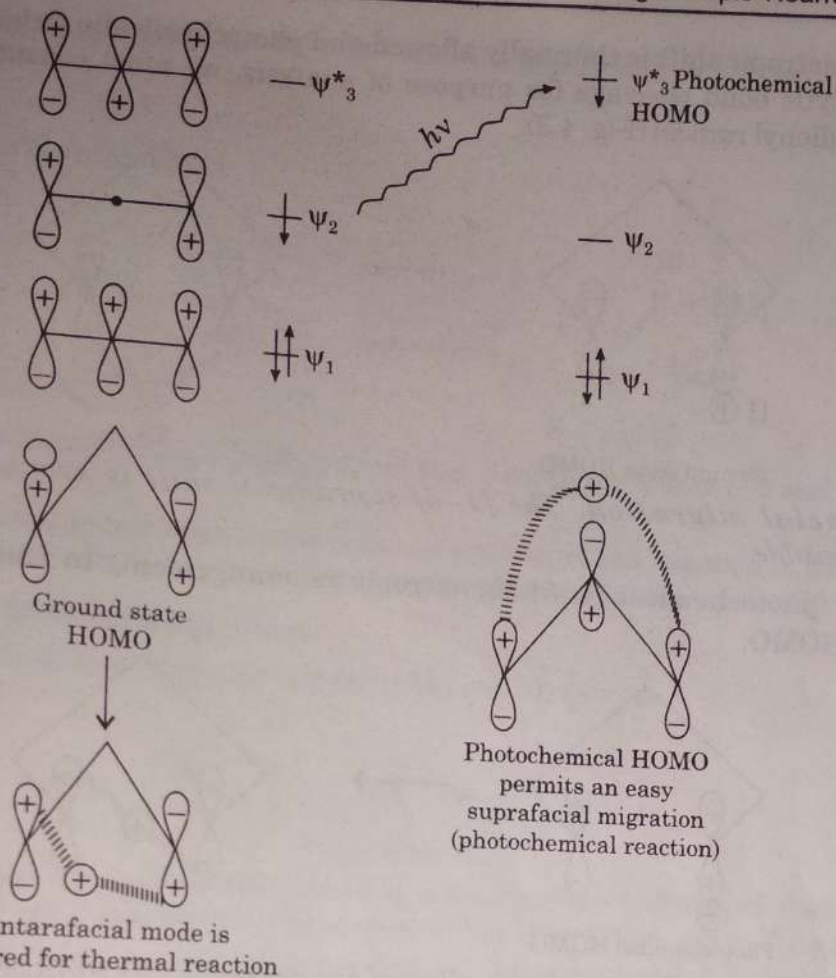
Ground state
HOMO

Antarafacial mode is
required for thermal reaction

Photochemical HOMO
permits an easy
suprafacial migration
(photochemical reaction)

Fig. 4.2 Suprafacial migration is possible in ψ^*_3 the photochemical HOMO of the reaction.
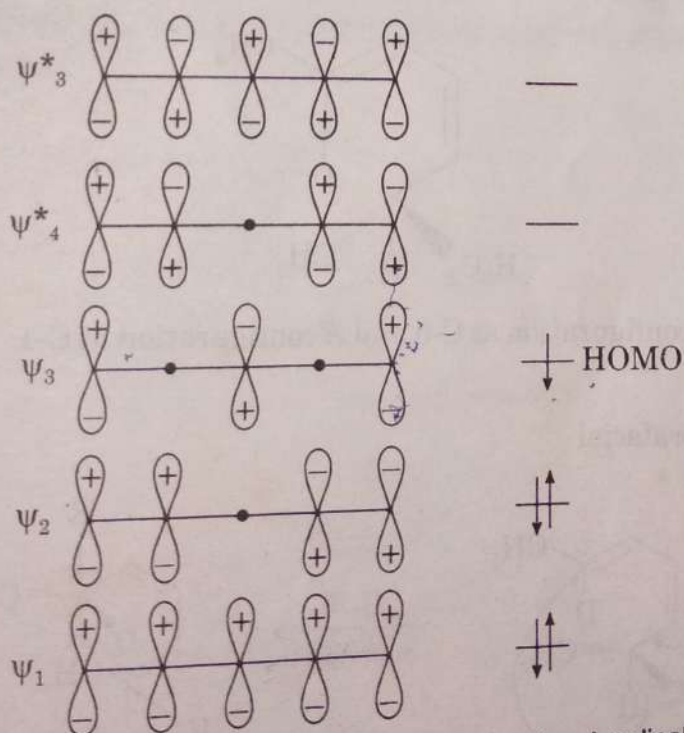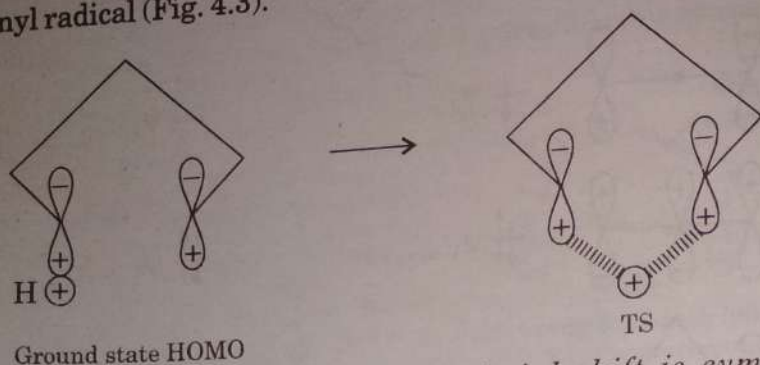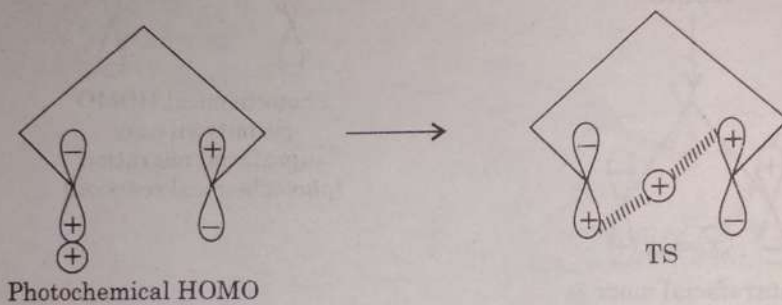
[1, 5] Sigmatropic Rearrangement

Fig. 4.3 π Molecular orbitals of the pentadienyl radical.

[1, 5] Sigmatropic shift is thermally allowed and photochemically forbidden. If we again assume a homolytic bond cleavage for purpose of analysis, we must consider the molecular orbitals of pentadienyl radical (Fig. 4.3).

Ground state HOMO

*Suprafacial migration. The [1, 5] suprafacial shift is symmetry allowed and geometrically feasible.*

Consider photochemical [1, 5] sigmatropic rearrangement. In this case ψ^*_4 will be photochemical HOMO.

Photochemical HOMO

Antarafacial migration, symmetry allowed but geometrically difficult.
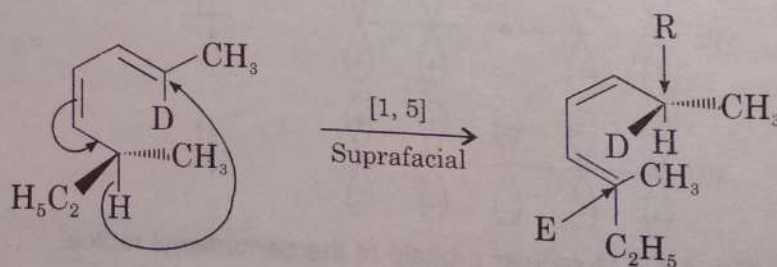
Stereochemistry of [1, 5] sigmatropic Rearrangement

Consider the following compound
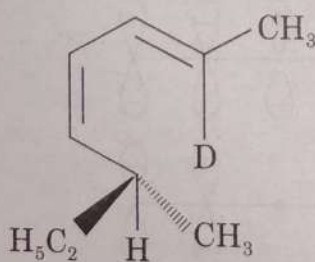
Compound has *S*-configuration at C-5 and *E* configuration at C-1
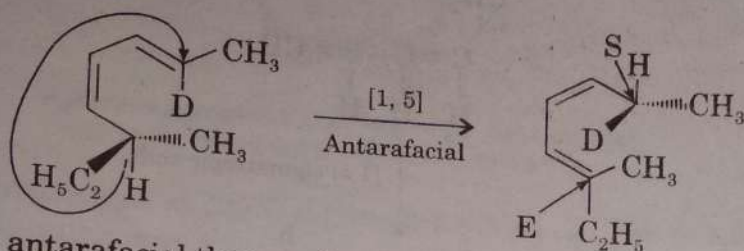
Case–I

Suppose migration is suprafacial

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

Case–II

Suppose migration is antarafacial

$$\xrightarrow[\text{Antarafacial}]{[1, 5]}$$

If migration is antarafacial then product has *S*-configuration at C-5 and *E*-configuration at C-1.

Experimentally it has been found that the product of the reaction is due to suprafacial migration. Thus the theory is confirmed by this experimental result.

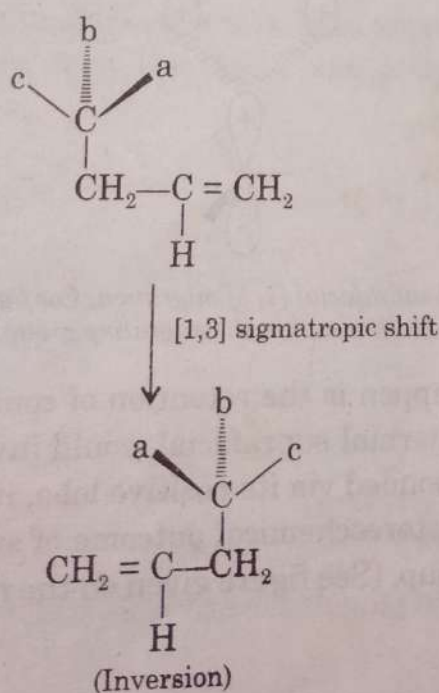### 4.2.1 Sigmatropic Shifts of Alkyl group

Sigmatropic migration involving alkyl group shifts can also occur.
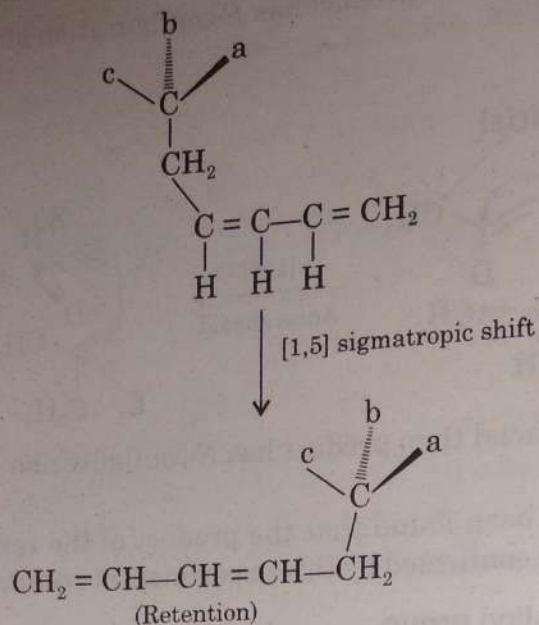

$$\xrightarrow{[1, 3]}$$

1,3–Alkyl shift
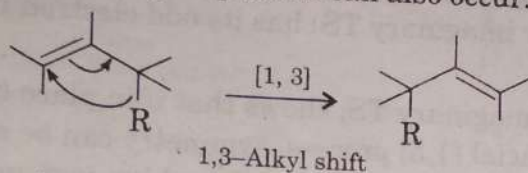
When an alkyl group migrates, there is additional stereochemical feature to consider. The shift can occur with retention or inversion at the migrating centre. The allowed process includes the suprafacial 1, 3-shift with inversion and the suprafacial 1, 5 shift with retention.

Thus if the group that migrates is bonded to the backbone by a **chiral** carbon, then :

1. [1, 3] suprafacial migration of the group proceeds with inversion of configuration at the chiral centre.

2. [1, 5] suprafacial migration of the group proceeds with retention of configuration at the chiral centre.

$$[1,3] \text{ sigmatropic shift}$$

(Inversion)

$$\underset{c}{\overset{b}{\underset{|}{C}}} \overset{a}{\diagup}$$

$$CH_2$$

$$\underset{H}{\overset{|}{C}} = \underset{H}{\overset{|}{C}} - \underset{H}{\overset{|}{C}} = CH_2$$

[1,5] sigmatropic shift

$$\underset{c}{\overset{b}{\underset{|}{C}}} \overset{a}{\diagup}$$

$$CH_2 = CH - CH = CH - CH_2$$
(Retention)

As compared to a hydrogen atom which has its electron in a $1s$ orbital that has only one lobe, a carbon free radical (for imaginary TS) has its odd electron in a p orbital which has two lobes of opposite sign.

A consideration of the imaginary TS, shows that if in place of hydrogen one has carbon, then during a thermal suprafacial [1,5] process, symmetry can be conserved only provided the migration carbon moves in a manner that the lobe which was originally attached to the *pi* system remains attached to it (see figure given below)
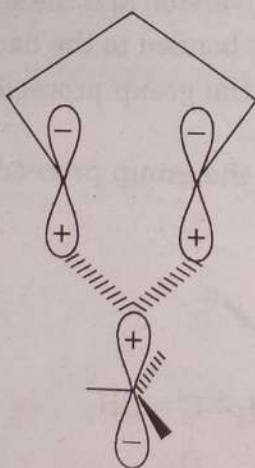
A thermal suprafacial [1, 5] migration. Configuration is retained within the migrating group.

The only way for this to happen is the retention of configuration within the migrating group. However, a related [1,3] thermal suprafacial would involve opposite lobes. Thus if the migrating carbon was originally bonded via its positive lobe, it must now use its negative lobe to form the new C—C bond. The stereochemical outcome of such a process is the inversion of configuration in the migrating group. (See figure given on the next page)

In this case migration occurs using the back lobe of migrating carbon, and now a bonding interaction is created. The migrating carbon suffers inversion as reattachment takes place to the position-3 of the allyl framework. In order to preserve bonding overlap with C-1 and C-3 rotation must occur, and the *trans* starting material is thus converted into *cis* product.

4.2.2 Selection Rules for Sigmatropic Rearrangement

The stereochemistry (*i.e.* migration of group is suprafacial or antarafacial) of sigmatropic rearrangement is a simply function of number of electrons involved (as with other pericyclic formalism: Simply count the curved arrow and multiply by two). All suprafacial sigmatropic reactions occurs when there are $(4q + 2)$ electrons involved in the reaction—that is an odd number of electron pairs or curved arrows.

Selection Rule of [1, n] Sigmatropic rearrangement when migrating group is hydrogen atom.

If sigmatropic reaction of the order $(m + n)$ (for hydrogen $m = 1$) has $m + n = 4q + 2$ then thermal reaction is suprafacial and photochemical reaction will be antarafacial. However, for those cases in which $m + n = 4q$ then thermal reaction is antarafacial and photochemical reaction will be suprafacial (Table 4.1)

Table 4.1 Selection Rule for $[1 + n]$ in which migrating group is hydrogen.

$m + n$	Thermal allowed Photochemical forbidden	$h\nu$ allowed Δ forbidden
$4q$	antara	supra
$4q + 2$	supra	antara

Table 4.2 Selection Rule for $[1 + n]$ in which migrating atom is carbon.

$m + n$	Δ allowed	$h\nu$ allowed
$4q$	ar	sr
	si	ai
$4q + 2$	sr	ar
	ai	si

In the table s and a refer to supra and antara and r and i refer to retention and inversion in the configuration of the migrating centre.

4.3   OTHER SIGMATROPIC SHIFTS

4.3.1 Cope Rearrangement

The most important sigmatropic rearrangement are the [3.3] process involving carbon-carbon bond. The thermal rearrangement of 1.5-dienes by [3,3] sigmatropy is called Cope rearrangement. The reaction proceeds in the thermodynamically favoured direction.

In this case migration occurs using the back lobe of migrating carbon, and now a bonding interaction is created. The migrating carbon suffers inversion as reattachment takes place to the position-3 of the allyl framework. In order to preserve bonding overlap with C-1 and C-3 rotation must occur, and the *trans* starting material is thus converted into *cis* product.

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If sigmatropic reaction of the order $(m + n)$ (for hydrogen $m = 1$) has $m + n = 4q + 2$ then thermal reaction is suprafacial and photochemical reaction will be antarafacial. However, for those cases in which $m + n = 4q$ then thermal reaction is antarafacial and photochemical reaction will be suprafacial (Table 4.1)

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$m + n$	Thermal allowed Photochemical forbidden	$h\nu$ allowed Δ forbidden
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$4q + 2$	supra	antara

Table 4.2 Selection Rule for $[1 + n]$ in which migrating atom is carbon.

$m + n$	Δ allowed	$h\nu$ allowed
$4q$	ar	sr
	si	ai
$4q + 2$	sr	ar
	ai	si

In the table *s* and *a* refer to supra and antara and *r* and *i* refer to retention and inversion in the configuration of the migrating centre.

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is that the reaction are concerted with relatively late transition state with well developed C–1–C–6 bonds (Figs. 4.5 and 4.6)

1,4-diradical   Two independent
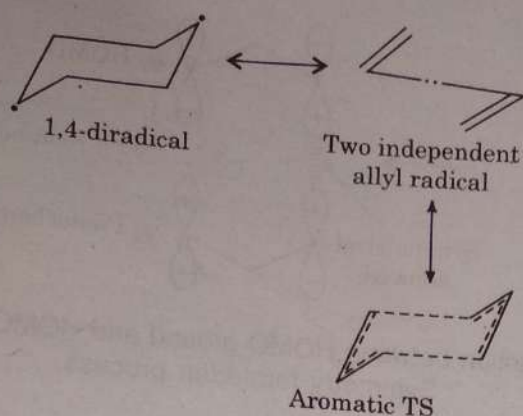   allyl radical

Aromatic TS

Fig. 4.6

The most advance molecular orbital calculations support the idea of an aromatic transition state having six partially delocalised electrons. The net effect on reaction rate of any substituent is determined by whether it stabilises the transition state or the ground state more effectively. The aromatic concept of transition state predicts that it could be stabilised by conjugated substituents at all positions.

In Cope rearrangement the migrating group is allyl radical. An analysis of the symmetry of the orbitals involved shows why this reaction is a relatively facile thermal process but is not commonly observed on photochemical activation. As we break the C(1) – C(1) bond (Fig. 4.7) the phases of the overlaping lobes must be the same. The HOMO of the allyl radical is ψ_2 (Fig. 4.1) and that information allows us to fill the symmetries of the two allyl radicals making up of transition state (Fig. 4.7).

TS   Migration of an
                allyl radical
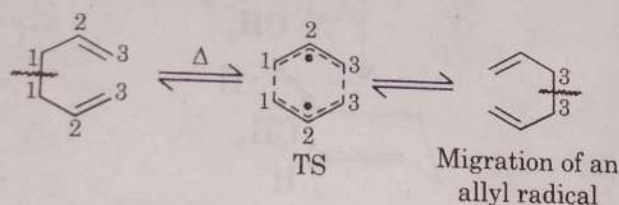
Fig. 4.7

Reattachment at the two C(3) positions (Fig. 4.7) is allowed because the interaction of the two lobes on the two C(3) carbons is bonding (Fig. 4.8).

Symmetry   Symmetry
allowed   allowed
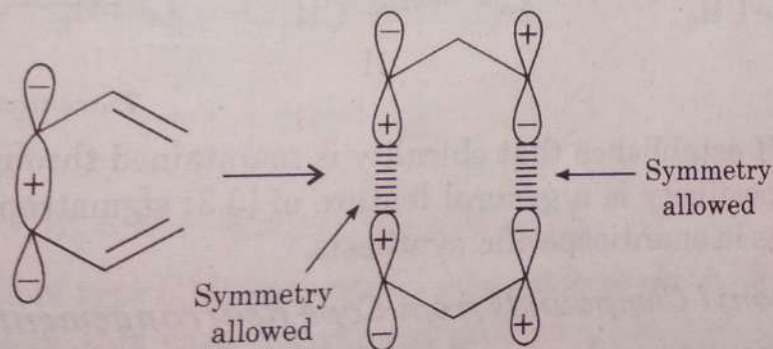
Fig. 4.8 Transition state: Two partially bonded allyl radicals-ψ_2 is the HOMO of each.

If interaction is carried out in the presence of UV light then one electron is promoted from the HOMO to the LUMO and LUMO will become photochemically HOMO (Fig. 4.9).
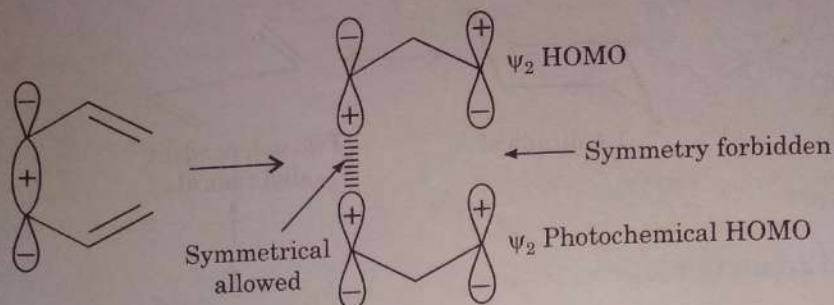

Fig. 4.9 Interaction between HOMO ground and HOMO photochemical. Symmetry forbidden process.

Stereochemistry of Cope Rearrangement

The Cope rearrangement usually proceeds through the chair like transition state. The stereochemical features of the reaction can usually be predicted and analysed on the basis of a chair transition state that minimises steric interactions between substituents. Rearrangement of the mesodiene through such transition state then would give the *cis-trans* isomer while in the case of the rearrangement of the *racemic* mixture the *trans-trans* isomer is the major product and this is actually the result.
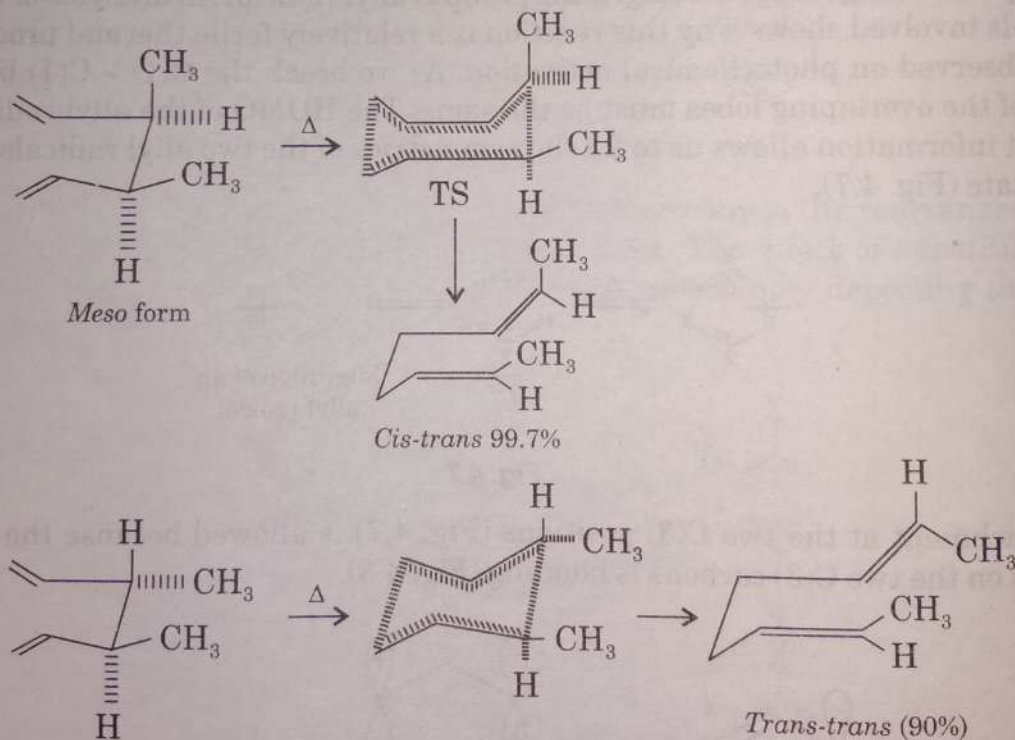
The above result establishes that chirality is maintained throughout the course of the reaction. This stereospecificity is a general feature of [3.3] sigmatropic shifts and has made them valuable reactions in enantiospecific synthesis.

Preparation of Carbonyl Compounds from Cope Rearrangement

1.5-Pentadien-3-ol on heating undergoes Cope rearrangement with formation of unsaturated carbonyl compounds. Cope rearrangement given by such compounds is known as oxy-Cope rearrangement.

Enol   Unsaturated carbonyl
                        compound
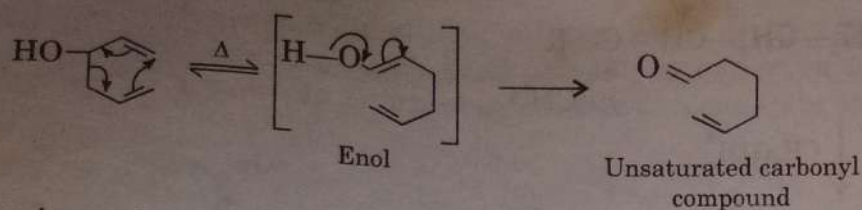
The reaction is accelerated when it is carried out in the presence of strong base. In the presence of strong base allyl alcohol converts into alkoxide ion which is very stable. Cope rearrangement given by anion of 1,5-pentadiene-3-ol is known as anionic oxy-Cope rearrange-ment.


Allyl alcohol   Anion of alcohol

Enolate ion   Product
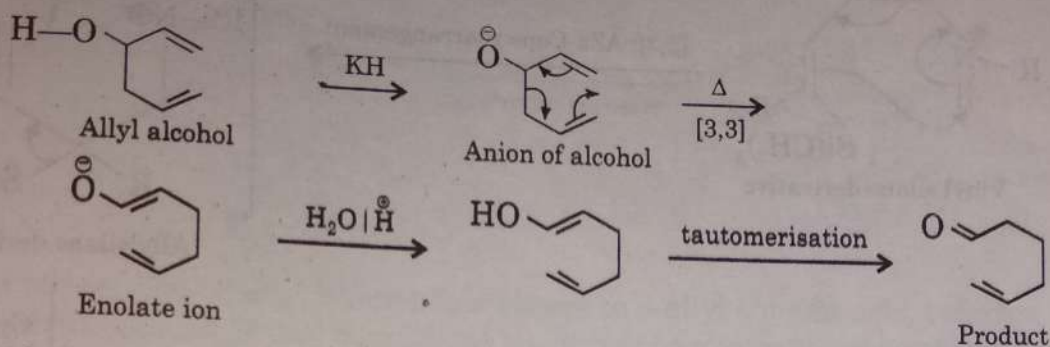
Alkoxide ion undergoes Cope rearrangement to give the product in which negative charge is in conjugation to *pi* bond. This conjugation makes the anion very stable.

Iminium compound of type (I) also gives Cope rearrangement. Which is known as AZ*a* Cope rearrangement.

(I)
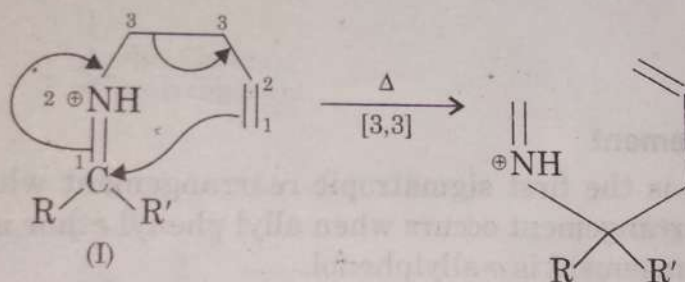
Compound (I) can be prepared from 4-aminoalkene.

$$H_2N—CH_2—CH_2—CH = CH_2$$
4-Aminoalkene
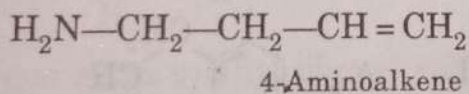
4-Aminoalkenes react with carbonyl compounds to give iminium compound of type (I).

$$H_2N—CH_2—CH_2—CH = CH_2$$

$$\downarrow CH_2O \mid \overset{\oplus}{H}$$

$$CH_2 = \overset{\oplus}{N}H—CH_2—CH_2—CH = CH_2$$
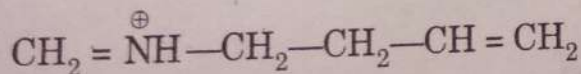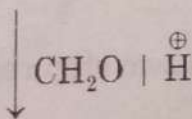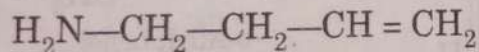
Iminium compound of type (I) is very useful when it is prepared from 4-(trimethylsilyl)-3-alkenylamines because in this case rearranged product undergoes cyclisation to give six membered nitrogen heterocyclic compound. Thus the overall reaction is as follows :

$$R'—NH—CH_2—CH_2—CH = \underset{\underset{Si(CH_3)_3}{|}}{C}—R$$

$$\downarrow CH_2O|H^{\oplus}$$

$$CH_2 = \overset{\oplus}{NH}—CH_2—CH_2—CH = \underset{\underset{Si(CH_3)_3}{|}}{C}—R$$

$$|||$$

Vinyl silane derivative

[3,3]; AZa-Cope rearrangement $\longrightarrow$



Allylsilane derivative

Cyclisation
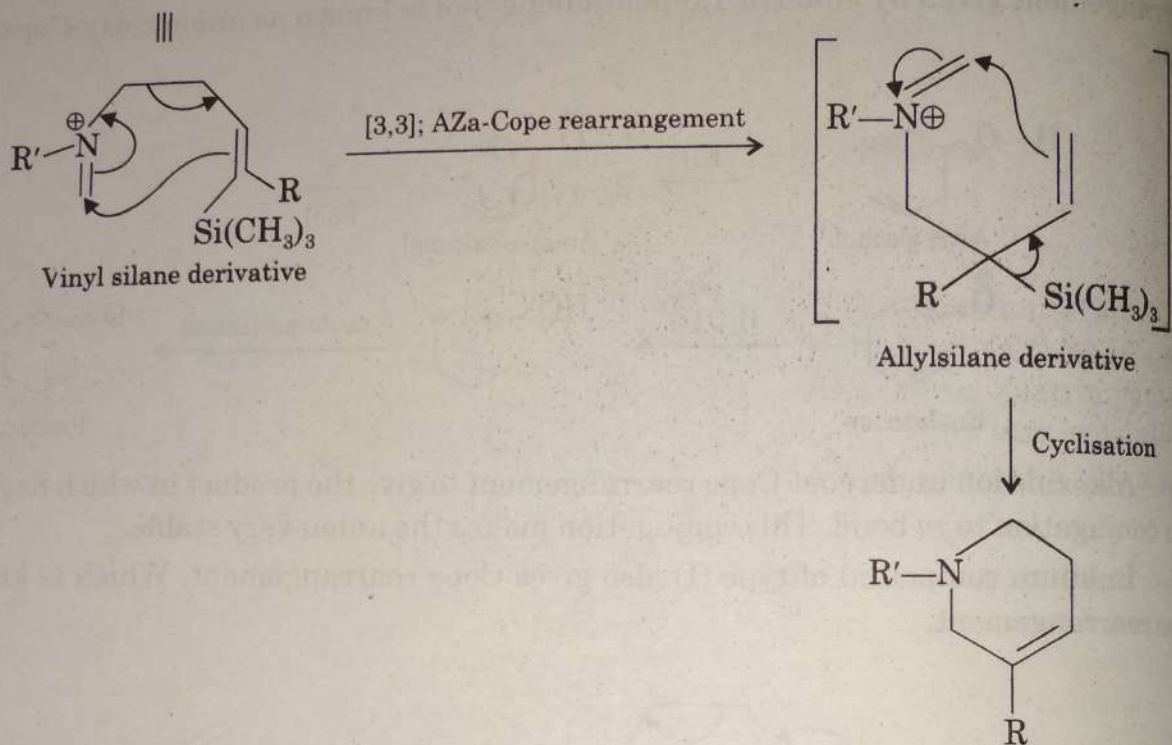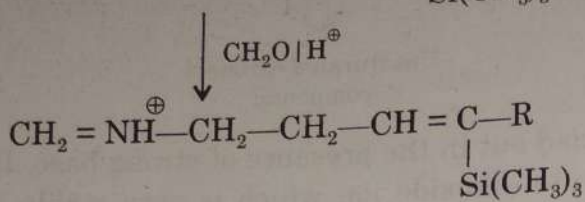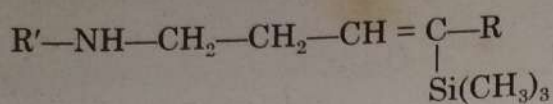
4.3.2 Claisen Rearrangement

Claisen rearrangement is the first sigmatropic rearrangement which was discovered. The original sigmatropic rearrangement occurs when allyl phenyl ether is heated without solvent. The product of the rearrangement is *o*-allylphenol.

o-Allylphenol
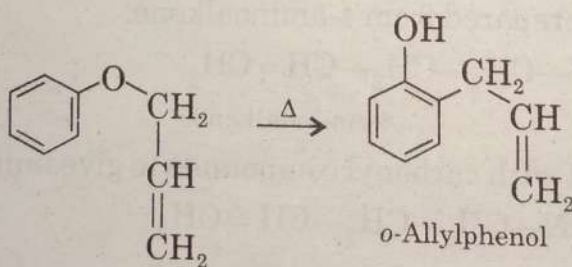
The above Claisen rearrangement is two step reaction. The first step in this reaction is [3.3] sigmatropic rearrangement
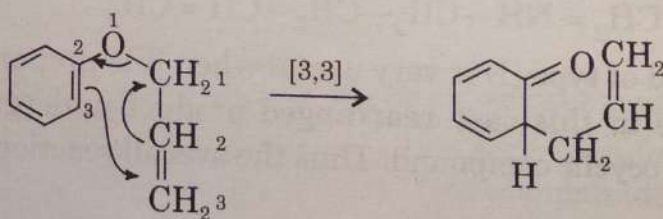
This is one step mechanism without ionic intermediates. In this case numbering start from the heteroatom oxygen having *sigma* bond and allylic carbon of the allyl group. The second step in the reaction is a simple ionic proton transfer to regenerate aromaticity.
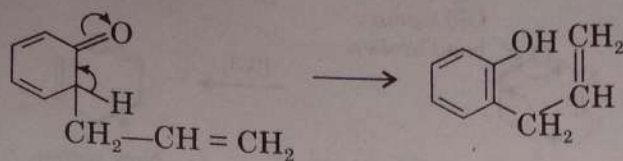
In this reaction allyl group turns inside out which is conformed by unsymmetrical allyl ether.
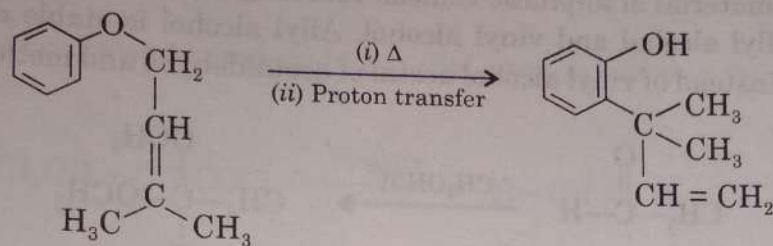

The conversion of allyl phenyl thio ethers to *o*-allyl thiophenols, referred to as the thio-Claisen rearrangement, is not possible as the latter compounds are unstable but they instead give bicyclic compound.
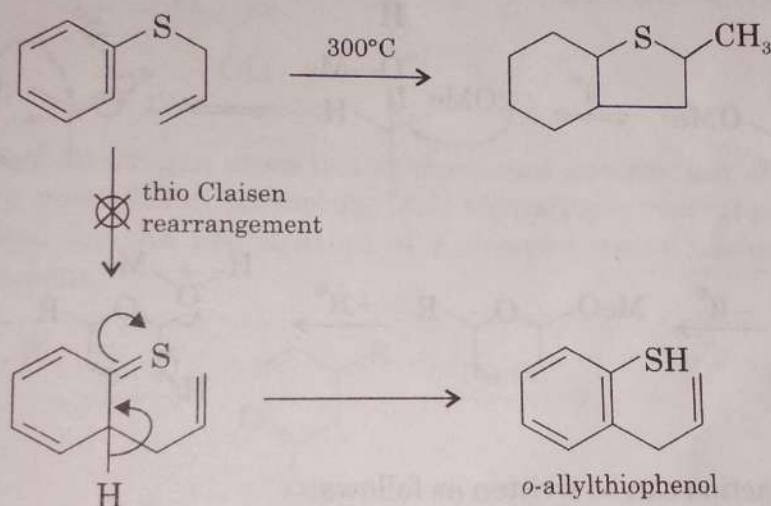
But if the oxygen atom in allyl phenyl ether is replaced by nitrogen, then the normal Claisen rearrangement takes place to afford the amino derivatives.

o-allylaniline
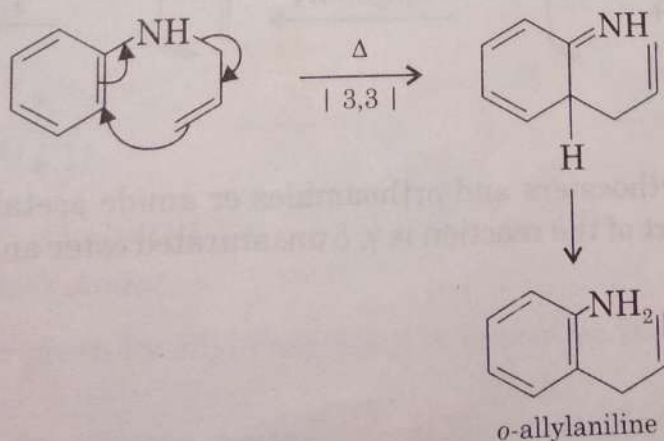
Claisen rearrangement is also given by allyl vinyl ether and in this case rearrangement is known as *aliphatic Claisen rearrangement* or *Claisen-Cope* rearrangement.
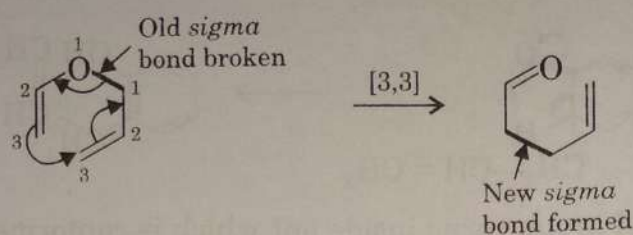

The starting material of aliphatic Claisen rearrangement is allyl vinyl ether which can be prepared with allyl alcohol and vinyl alcohol. Allyl alcohol is stable compound but vinyl alcohol is not. Thus instead of vinyl alcohol acetal of acetaldehyde and methyl alcohol is used.
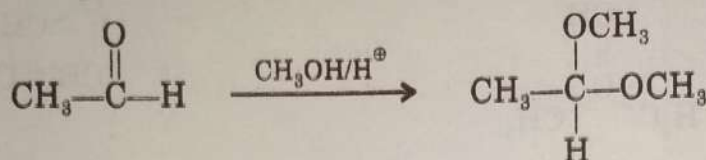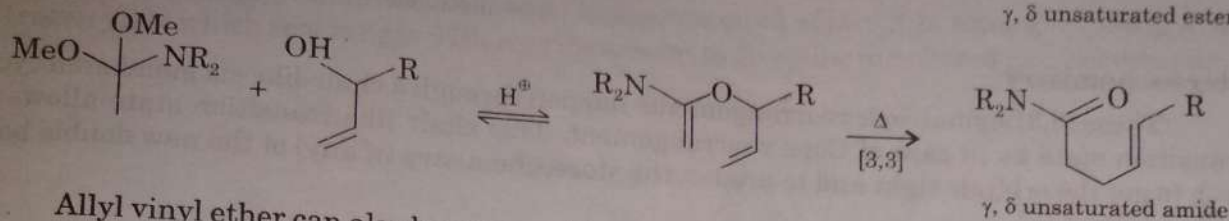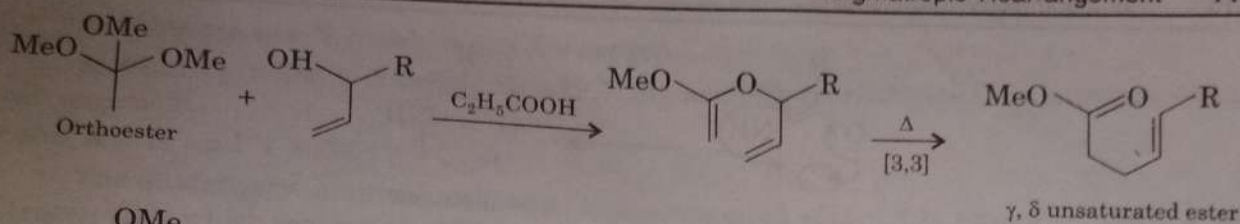

When this acetal is treated with allyl alcohol, formation of vinyl allyl ether takes place.
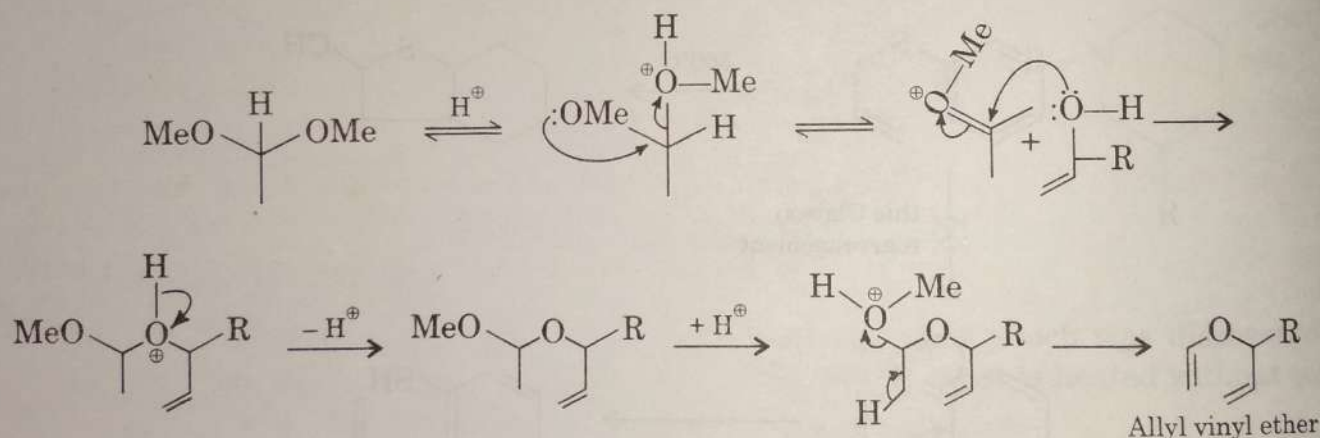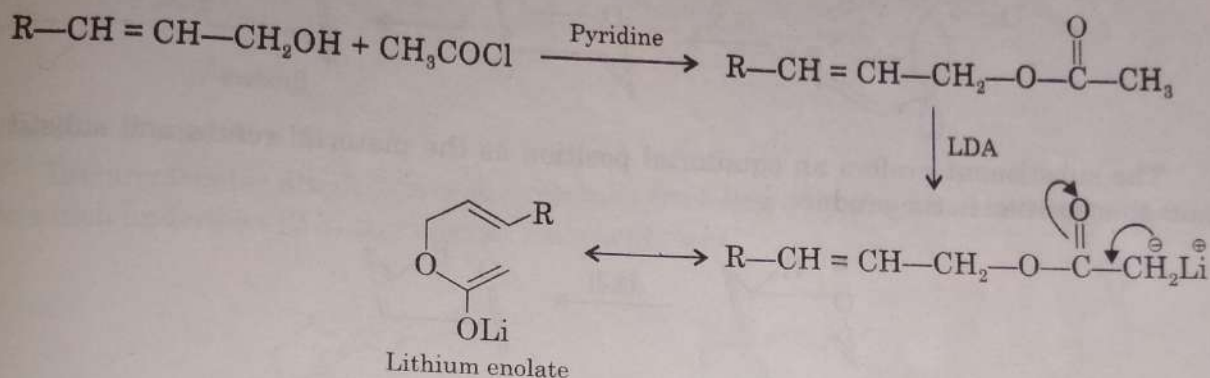

Thus overall reaction can be written as follows:
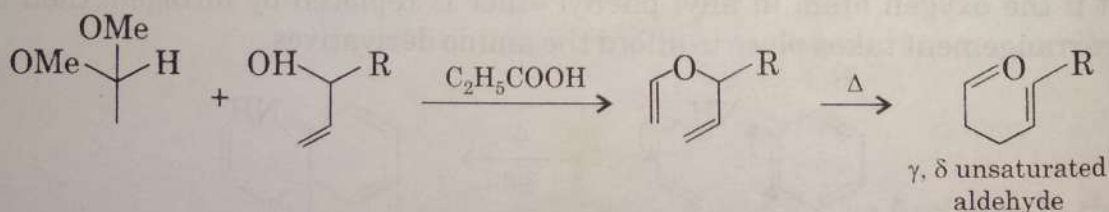
In this reaction orthoesters and orthoamides or amide acetals can be used in place of acetal or ketal and product of the reaction is γ, δ unsaturated ester and amide respectively.

γ, δ unsaturated ester

γ, δ unsaturated amide

Allyl vinyl ether can also be prepared from allyl alcohols and acid chlorides.

$$R—CH = CH—CH_2OH + CH_3COCl \xrightarrow{\text{Pyridine}} R—CH = CH—CH_2—O—\overset{\overset{\displaystyle O}{\|}}{C}—CH_3$$

$$\Big\downarrow \text{LDA}$$

$$\longleftrightarrow R—CH = CH—CH_2—O—\overset{\overset{\displaystyle O}{\|}}{C}—\overset{\ominus}{C}H_2\overset{\oplus}{Li}$$

Lithium enolate

A combination of an oxygen atom in the chain and another out of the chain (at inner vinylic carbon) is very powerful at promoting [3,3] sigmatropic rearrangement. Such type of compound can be used for the preparation of γ, δ-unsaturated carboxylic acid *via* [3,3] sigmatropic rearrangement.


γ,δ-unsaturated acid
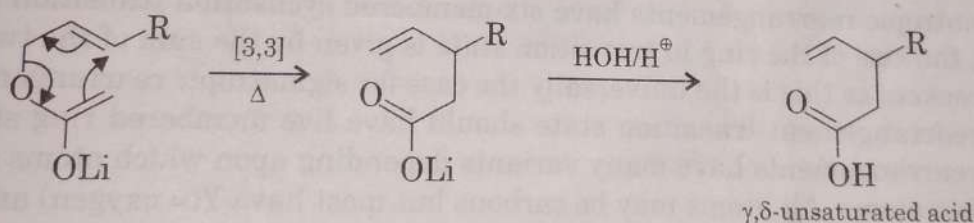
Sometimes it is better to convert the lithium enolate into the silyl enol ether before [3,3] sigmatropic rearrangement.


Silylenol ether

γ,δ-unsaturated acid
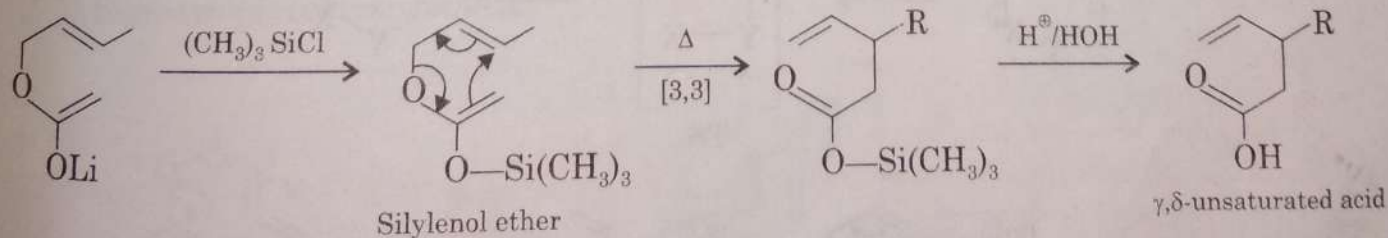
Cope rearrangement given by silyl enol ether is known as *Ineland-Claisen* rearrangement.

o-Allyl imidates also give Claisen rearrangement known as AZα-Claisen rearrangement.

N-allylamide
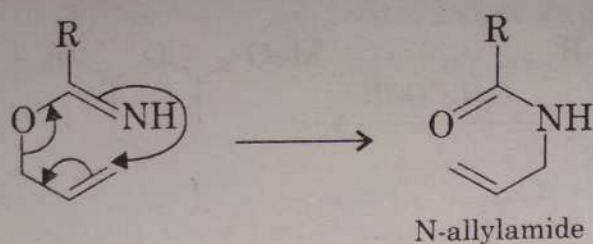
Stereochemistry

These [3,3] sigmatropic rearrangements happen through a chair-like six membered cyclic transition state as in case of Cope rearrangement. This chair like transition state allows us both to get the orbitals right and to predict the stereochemistry (if any) of the new double bond in the product.
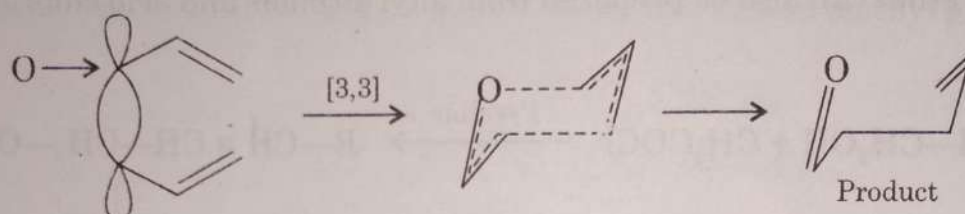
Product

The substituent prefers an equatorial position as the material reacts and substituent retains this position in the product.
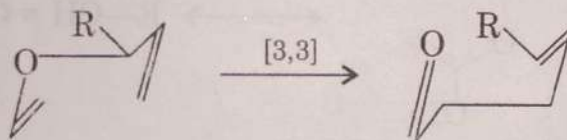
Thus the resulting double bond strongly favours *trans* (*E*) geometry.

Group Transfer Reactions

A pericyclic process involving the transfer of one or more groups or atoms from one molecule to another is known as group transfer reaction. There are only a few reactions in this class. *Ene* reaction is one of the most common group transfer reaction. The other well known group transfer reaction is reduction of alkenes and alkynes by diimide.

5.1   ENE REACTIONS

Ene reaction involves the thermal reaction of an alkene (called ene) having an allylic hydrogen with a compound having multiple bond (X = Y, X ≡ Y), called enophile.

During the reaction, transfer of allylic hydrogen (1,5 migration of hydrogen), shift of allylic double bond and bonding between two unsaturated termini (one terminus of ene and other terminus of enophile) takes place to form 1 : 1 adduct.

ene   enophile   Adduct   (i)
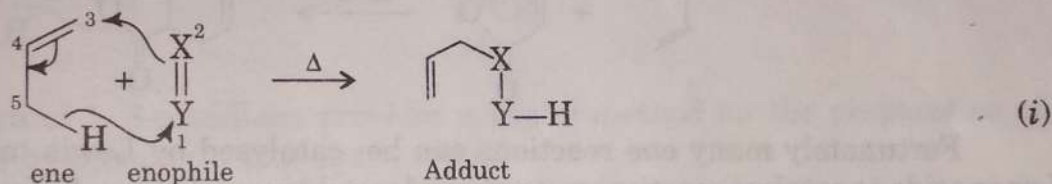
In this reaction

| X = Y is	X ≡ Y is
C = C	C ≡ C
C = O	C ≡ N
C = S	
C = N	
N = O	
—N = N—	
O = O	

In ene reaction hydrogen atom of allylic carbon moves from ene to enophile. In principle atom other than hydrogen from allylic carbon can move from ene to enophile. In practice the only elements other than hydrogen commonly employed in this kind of reaction are metals like lithium, magnesium or palladium. When metal moves the reaction is known as *metalla–ene* reaction.

(ii)

Adduct
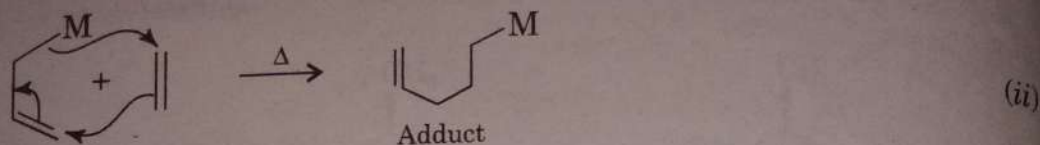
In ene reaction there is a loss of a *pi* bond and gain of two *sigma* bonds. In this reaction *pi* bond of enophile is replaced by two *sigma* bonds with ene, therefore, this reaction resembles with cycloaddition reaction. This reaction also resembles with [1,5] sigmatropic rearrangement because hydrogen migrates on atom – 5 (equation – 1) but reaction is neither sigmatropic nor cycloaddition reaction. This reaction is six electrons cycloaddition reaction. In this reaction hydrogen moves from ene to enophile. Due to this reason reaction is an example of group transfer reaction. This reaction is like Diels-Alder addition. In Diels-Alder addition all six electrons are *pi* electrons. In this reaction, out of six electrons, four electrons are *pi* electrons but two electrons are *sigma* electrons. Thus activation energy of this reaction is greater than the Diels-Alder reaction. Due to this reason ene reactions take place at higher temperature than Diels-Alder reaction.


(iii)

(iv)
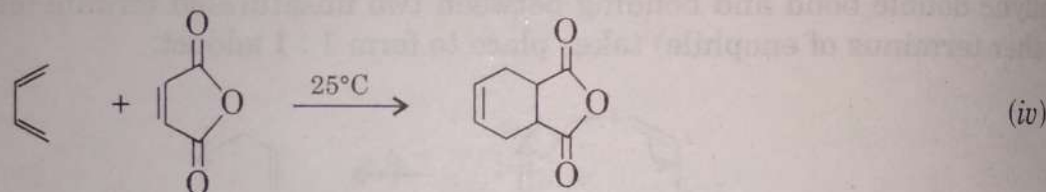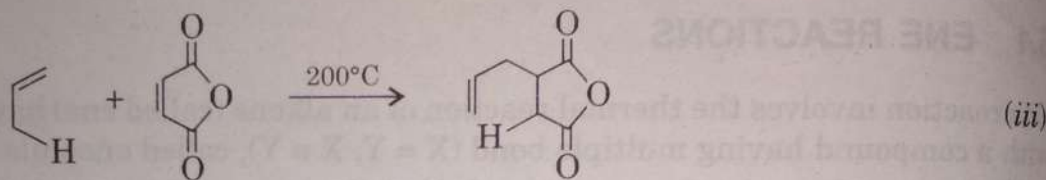
Fortunately many ene reactions can be catalysed by Lewis acids. In the presence of Lewis acids as catalyst reaction proceeds under milder conditions. As far as catalyst is concerned the best result is obtained with alkyl aluminium halides.


(v)
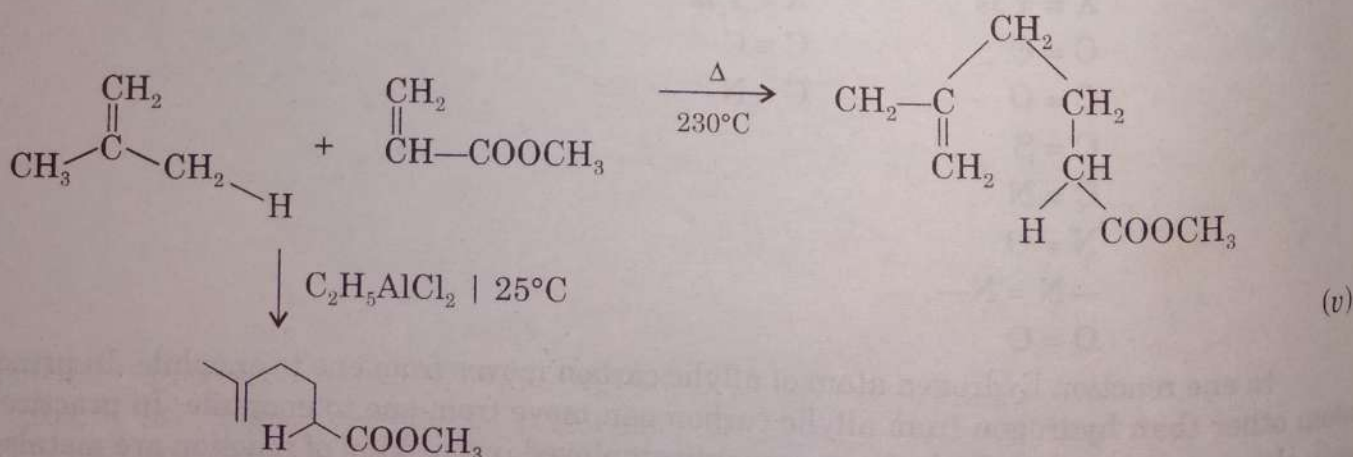
Like Diels-Alder addition ene reaction is also reversible reaction. 1–Pentene gives ethene and propene at 400°C

(vi)
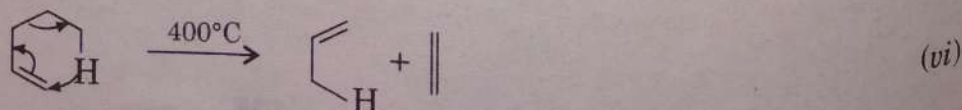
As mentioned earlier that enophile need not be alkene or alkyne derivatives heteroeno-
philes are also known.

(vii)

(viii)

(ix)
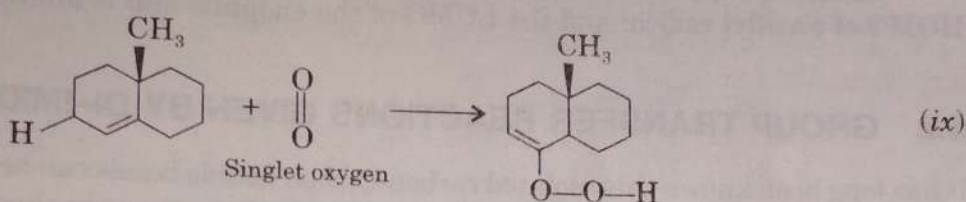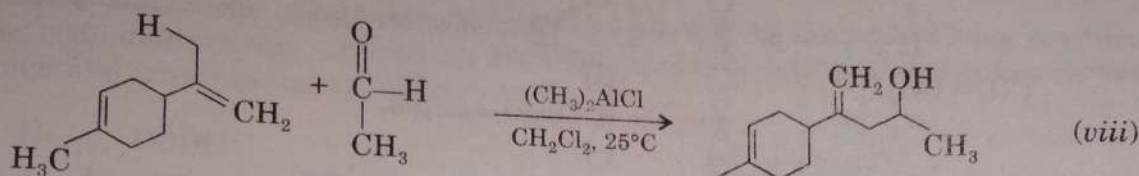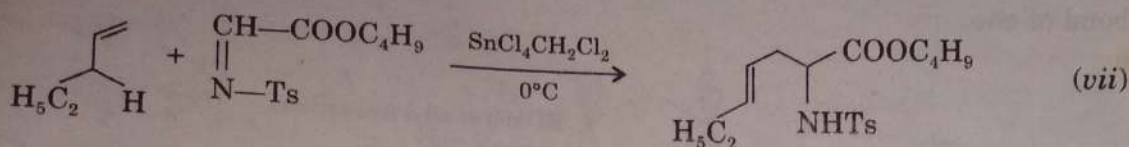
Intramolecular ene reaction has great potential for the synthesis of cyclic compounds,
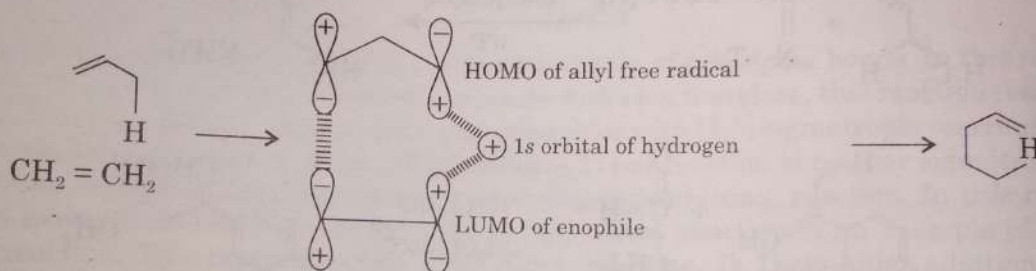particularly for the synthesis of five membered ring compounds from 1, 6-dienes.

(x)
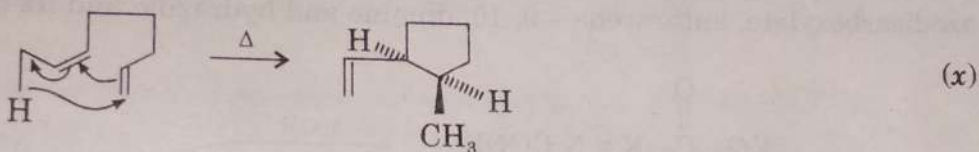
Thermal cyclisation of 1, 8-alkadiene provides a useful method for the preparation of
cyclopentyl vinyl ketones by intramolecular ene reaction.

(xi)
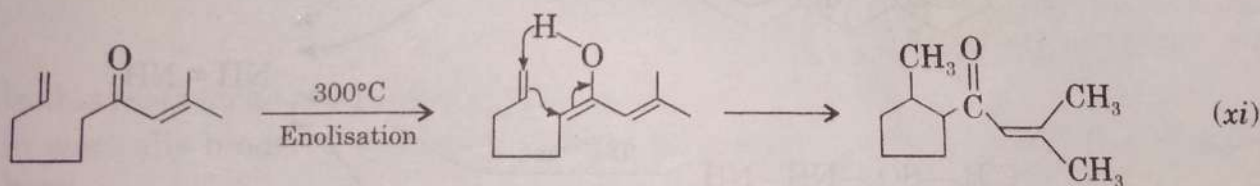
Similarly 7, 9-alkadienone gives intramolecular ene reaction.

(xii)
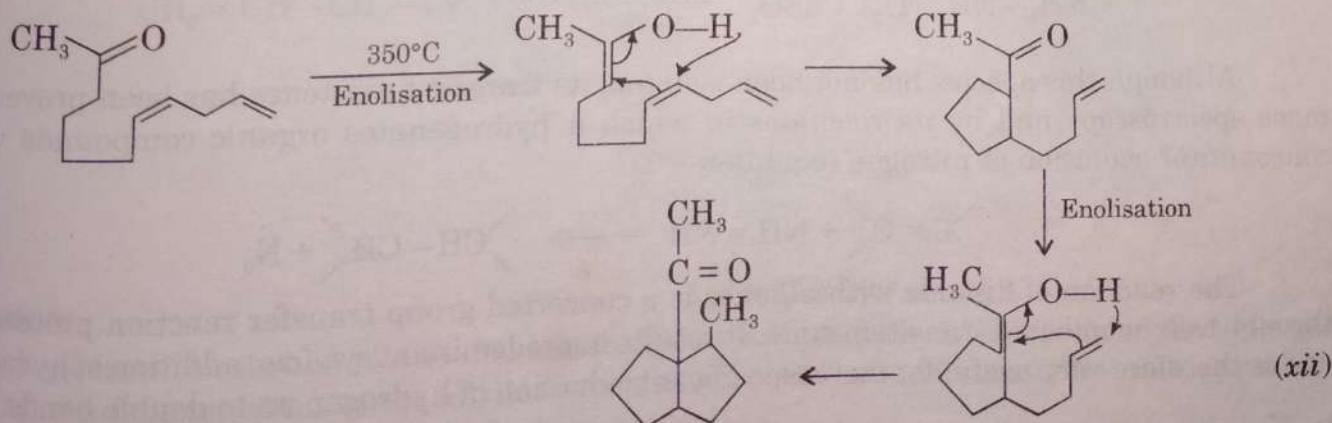
The concerted mechanism is allowed by Woodward-Hoffmann rules. The transition state involves the *pi* electrons of the ene and enophile and the *sigma* electrons of the C—H bond of ene.

HOMO of allyl free radical

$1s$ orbital of hydrogen

LUMO of enophile

$CH_2 = CH_2$

H

A concerted ene reaction corresponds to the interaction of a hydrogen atom with the HOMO of an allyl radical and the LUMO of the enophile and is allowed.