Subject	Chemistry
Paper No and Title	1: ORGANIC CHEMISTRY- I (Nature of Bonding and Stereochemistry)
Module No and Title	30: Chirality Axis- Stereochemistry of Allenes
Module Tag	CHE_P1_M30

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1. Learning Outcomes

After studying this module, you shall be able to

- Know the axial chirality in allene.
- Know the structure and point group of the allenes.
- Distinguish between asymmetric and dissymmetric allenes.
- Determine the absolute configuration from the structure.
- Analyse various methods of synthesis of allenes.
- Identify the enantiomers of the allenes.

2. Introduction

2.1 Allenes: An Introduction

Certain stereoisomers which does not possess center of chirality (stereoisomers of allenes, atropisomerism of biphenyl and ansa compounds) but they are chiral and two additional stereogenic units were introduced in 1956 i.e. chirality plane and chirality axis. As early as 1875, Van't Hoff pointed out that an appropriately substituted allene should exist in enantiomeric forms.

Chirality Axis: An axis about which a set of substituents is hold in a spatial arrangement that is not supposable to its mirror image. The simple principles for the chirality axis and chirality plane have recently been refined by Prelog and Helmchen (1982) as elongated (extended) tetrahedral approach.

2.2 Elongated tetrahedral approach

A regular tetrahedron with four distinguishable vertices (structure **A** in figure 1) represents a three dimensional chiral simplex. The central tetrahedron which is usually occupied by a tetracoordinate atoms e.g., C in Cabcd. If this centre is replaced by a linear grouping such as C-C or C=C=C, the tetrahedral becomes elongated along the axis of the axis shown in **B** in allene abC=C=Cab. Such elongated tetrahedron (D_{2d} point group with $3C_2$ axes and 2σ planes) has lesser symmetry than a regular tetrahedral (T_d) and condition for desymmetrisation is less stringent instead of all the four vertices are distinguishable. In the case of allene of only pair of vertices of two ends of the axis need to be distinguishable (a ≠ b). The axis along with tetrahedral is elongated called the chiral axis or the stereo axis.

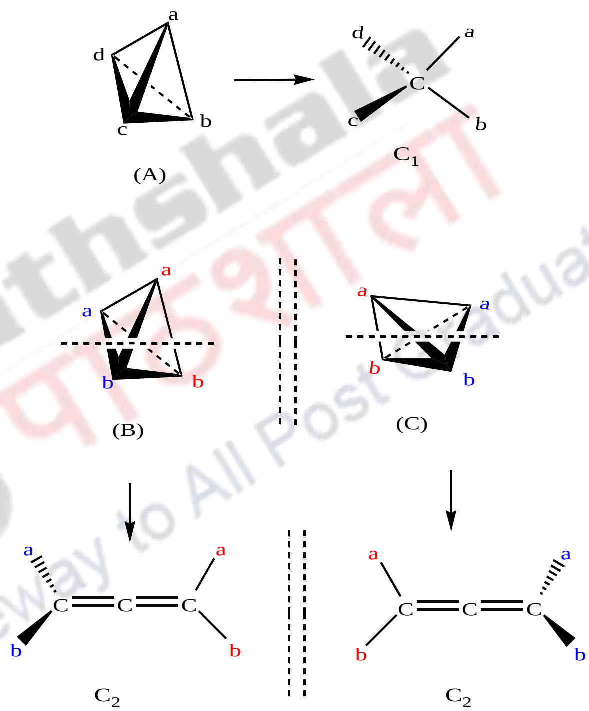
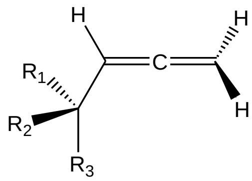


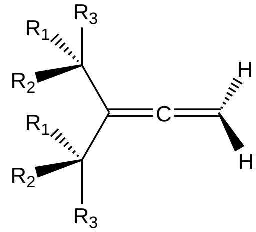
Fig. 1: Elongated tetrahedral in allene

2.3 Types of allenes:

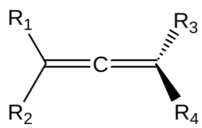
1. **Asymmetric allenes:** Allenes having an asymmetric carbon or C_1 point group is classified as asymmetric allene



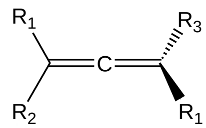
$R_1 \neq R_2 \neq R_3$



$R_1 \neq R_2 \neq R_3$

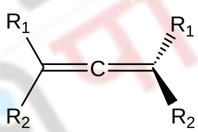


$R_1 \neq R_2 \neq R_3 \neq R_4$

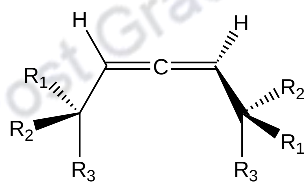


$R_1 \neq R_2 \neq R_3$

2. Dissymmetric allenes: Allenes having C_2 point group known as dissymmetric allenes.



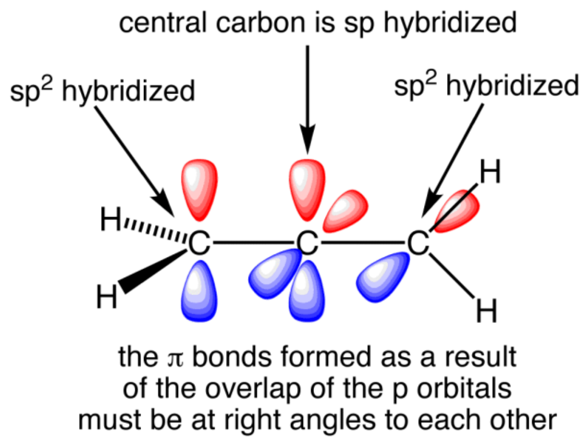
$R_1 \neq R_2$



$R_1 \neq R_2 \neq R_3$

2.4 Structure and hybridization in allene

Hybridization in allene for central carbon is sp and two terminal (edge) carbon atoms are sp^2. The hybridization of central sp hybrid carbon atom must use two different p-orbital to from Π-bond with two edge carbon atom. In this two Π-bonds are perpendicular to each other (Figure 2).



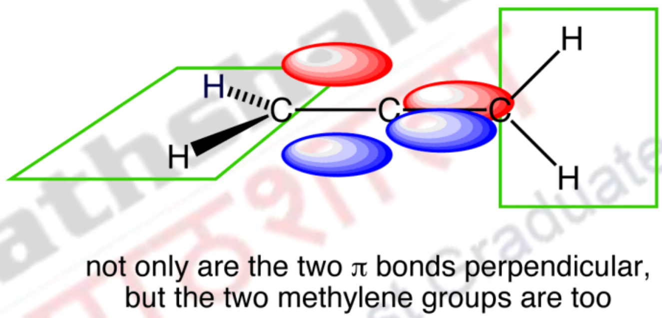


Fig. 2: P-Orbital overlapping in allene;
Source : http://www.chemtube3d.com/orbitalsallene.htm

2.5 Point group symmetry in allenes

1. We have learned that allene has two π-bond perpendicular to each other

2. It has three C_2 axes (a) passes through three carbon atoms of the allene; (b) passes through central carbon of allene; (c) passes through central carbon of allene perpendicular to earlier axis (Figure 3 and 4)

3. It has one improper axis (S_4), it passes through three carbon atoms of the allene and plane is perpendicular to this (Figure 5). The rotation of 90° and then reflection through plane gives indistinguishable allene (i.e. S_4).

4. It also contains two σ-planes (I e dihedral planes) given in figure 5.

5. The point group of allene is D_{2d}.

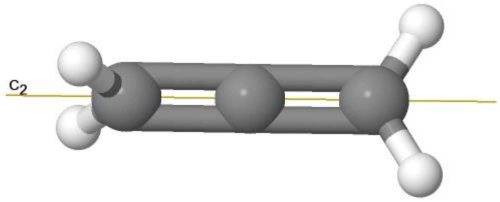


Fig.3: Principle axis in allene (C_2) passes through three carbon atoms

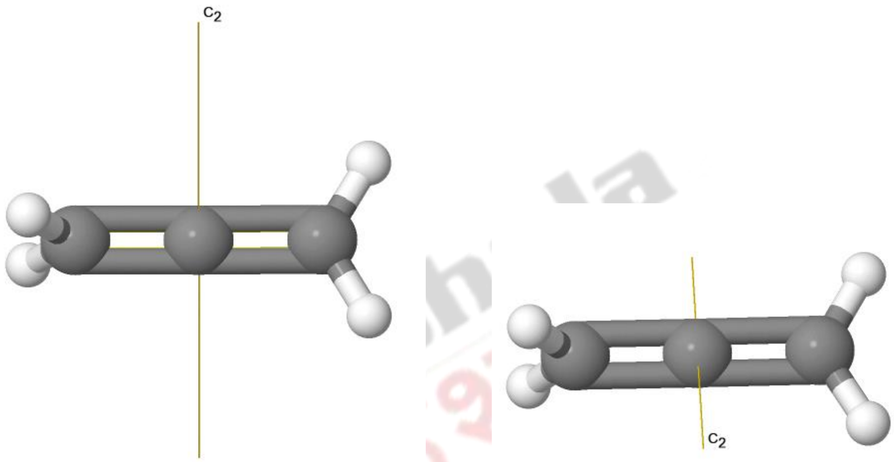
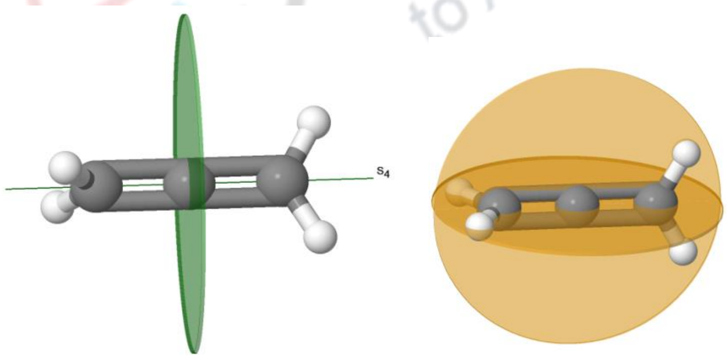


Fig. 4: Principle axes in allene

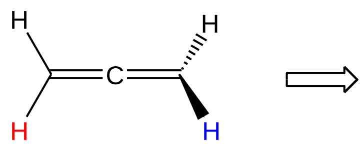


(A) **(B)**

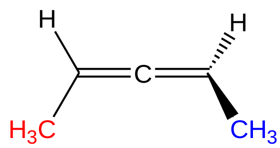
Fig. 5: S_4 axis in allene (A) and 2 dihedral planes (B) and Point group is D_{2d}

Conditions for chirality:

1. Allene (1,2-propadiene) has point group D_{2d}, itself is achiral because it has two planes of symmetry. It could be chiral if plane of symmetry is eliminated by substitution of terminal carbon atoms are different (If H is replaced by CH_3).

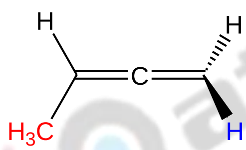


Achiral



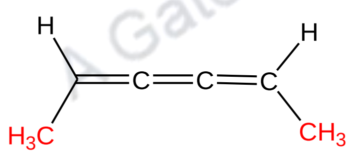
Chiral

2. An allene with substituents on one terminal carbon atom are unlike and substituent on other terminal carbon atoms are same, allene will be achiral. It will have one symmetry plane.



Achiral

3. The Cumulene with odd number of double bond with terminal carbon atoms having unlike substituent also will be achiral because both terminal planes will be same.



Achiral

2.6 Allenes in natural products

Allenes are interesting molecules and this core structure was found in many of natural products. We have shown some structure where allene is core unit in natural products which is shown in figure 6. First naturally occurring allene, pyrethrolone, characterized by **H. Staudinger** and **L. Ruzicka** (*Helv. Chim. Acta* **1924**, *7*, 177).

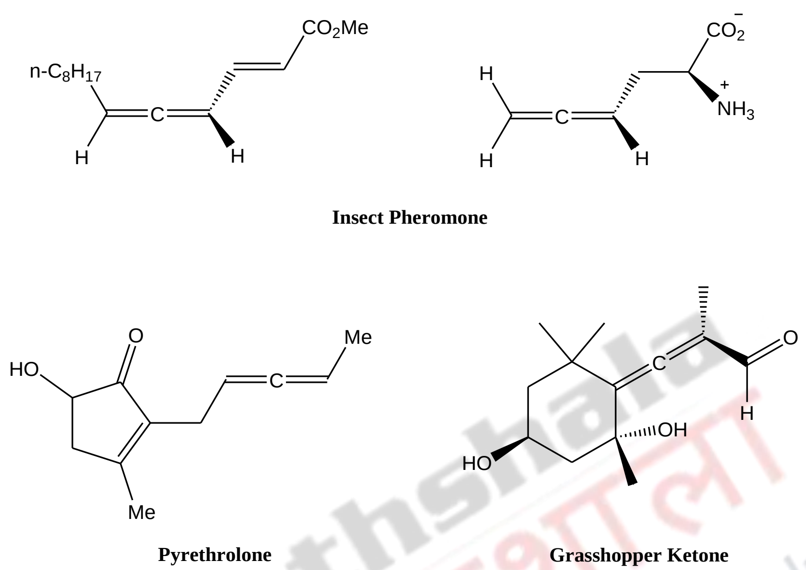


Fig. 6: Natural products containing allenes

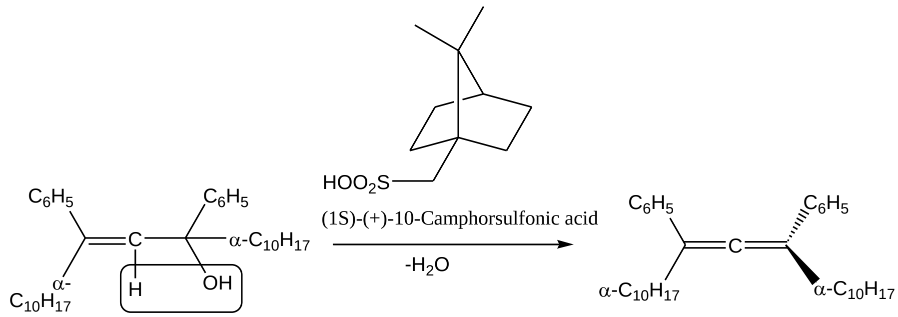
2.7 Synthesis of optical active allenes

Nowadays, about 150 natural products comprising an allenic or cumulenic structure are known. The chemistry of these compounds has turned out to be a very attractive and prolific area of interest: advances in the isolation and characterization of new allenic natural products have led to the establishment of efficient synthetic procedures which in many cases also open up an access to enantiomerically pure target molecules.

1. Dehydration of allylic alcohols

The first optically allene was prepared by Maitland and Mills (1935) sixty years after Van't Hoff's prediction. 1,3-Diphenyl-1,3-di-alpha-naphthyl-2-propen-1-ol was dehydrated with (+) and (-) and (±)-camphor-10-sulphnic acid respectively

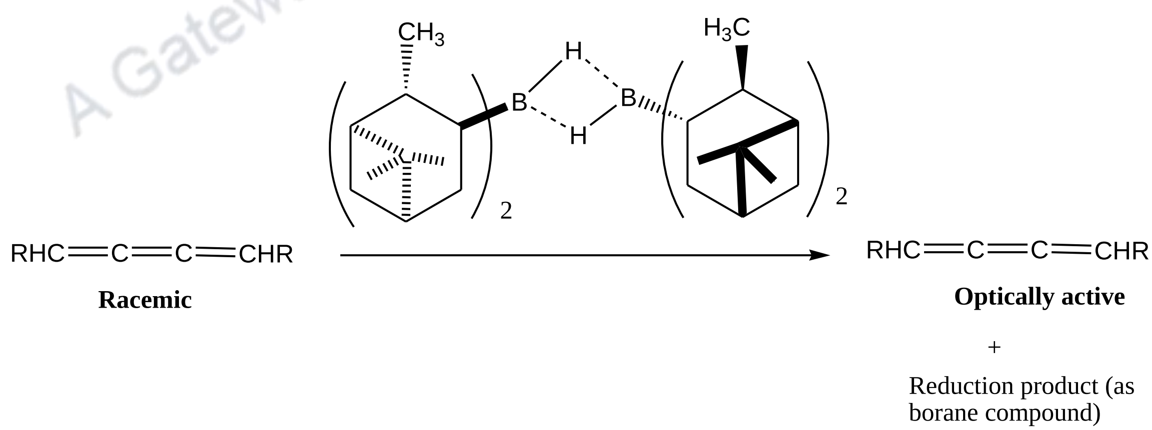
(Scheme 1). With (±)-camphor-10-sulphnic acid the allene was obtained as racemic while with (+)-sulphonic acid slight enantiomeric (3%) was obtained.



Scheme 1. Synthesis of optically active allene

2. Kinetic resolution of chiral allenes

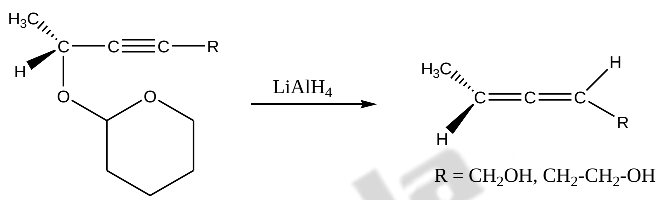
The optically active allene can be synthesized by kinetic resolution of racemic compound. Racemic compound is the mixture of equimolar amount (50:50) of enantiomers. In the kinetic resolution one enantiomer reacts faster than other enantiomer. One enantiomer react fast gives the product and slow reactive enantiomer will be as it is in the reaction mixture. The Kinetic resolution of racemic allene with chiral hydroboration reagent (Ipc_2BH) gives the reduction product as borane compound and optically active allene was found to be unreacted during the kinetic resolution (Scheme 2)



Scheme 2. Kinetic resolution of racemic allene

3. Reductive rearrangement of chiral acetylenic carbinol

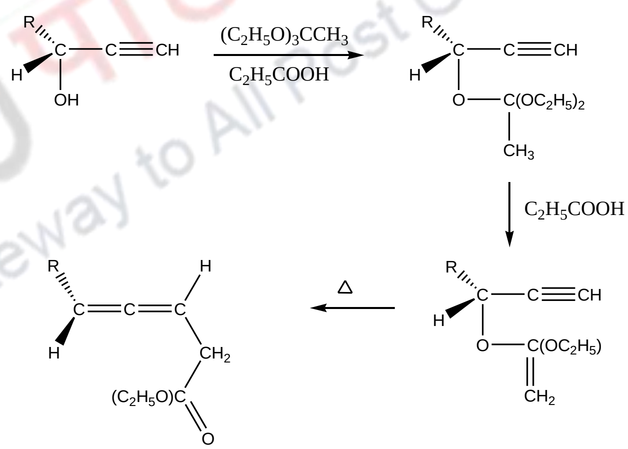
In this synthesis the ether of optically active acetylenic carbinol is treated with $LiAlH_4$ (reductive reagent) give the enantioselective allene. The addition of hydride is *trans* and hydride approaches to acetylene from opposite side of the –OTHP leaving group.



Scheme 3: Reductive rearrangement

4. Ortho ester Claisen rearrangement

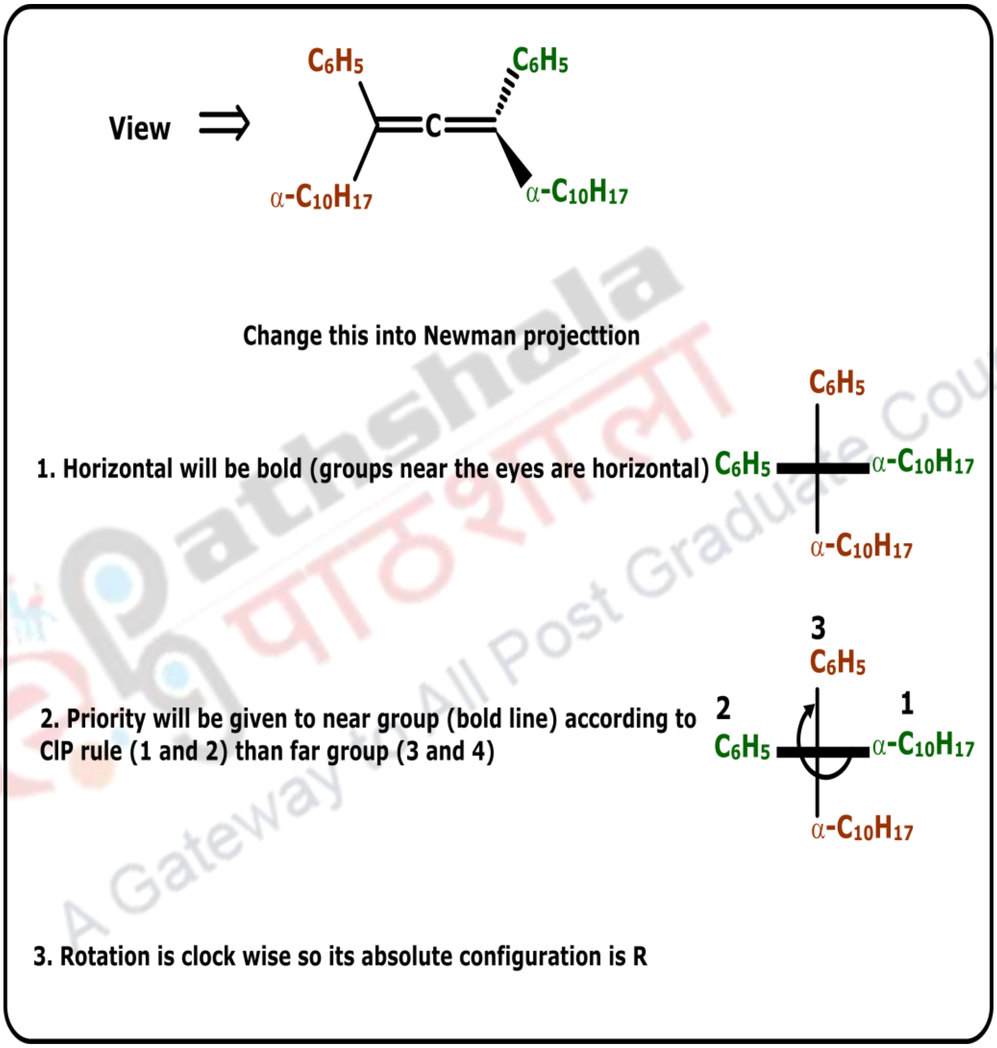
In 1988, Mori et al prepared the enantioselective allenes for the synthesis of the sex pheromones produced by male dried-bean beetle (Scheme 4)



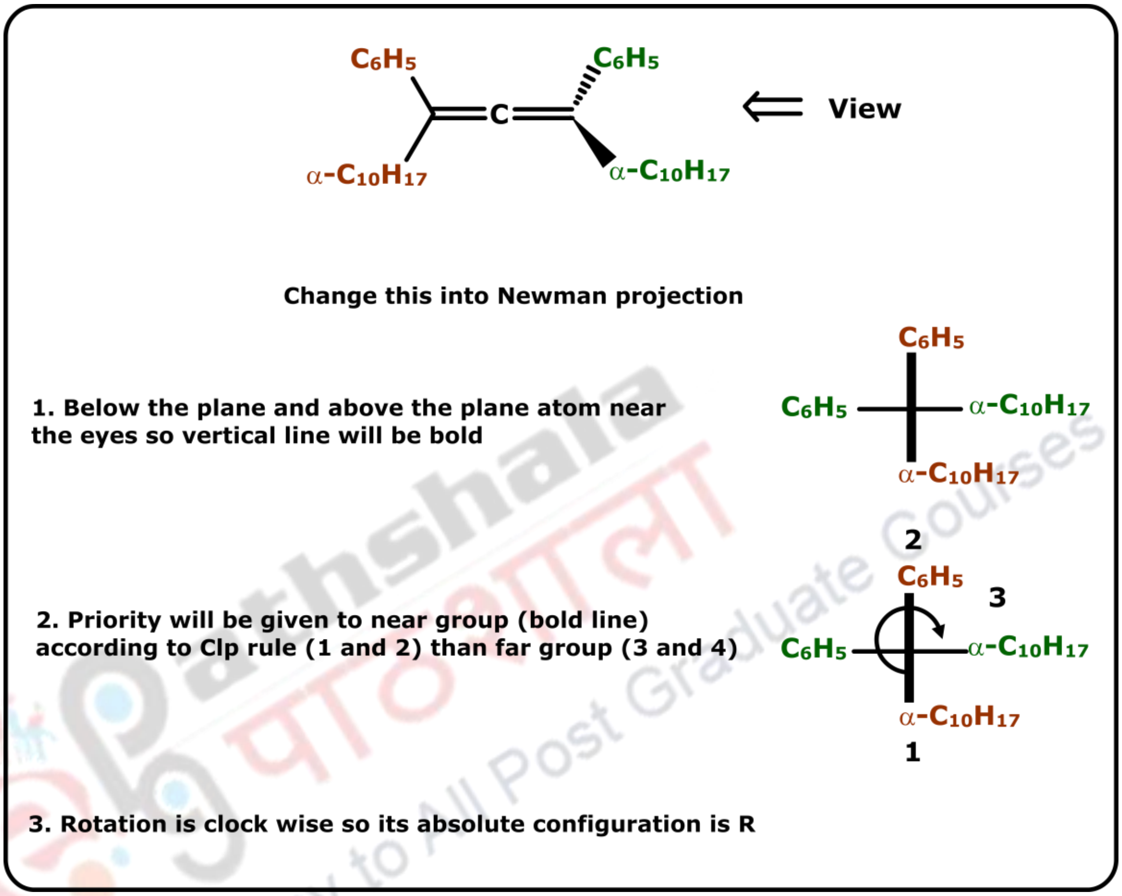
Scheme 4: Ortho ester Claisen rearrangement

2.8 How to assign R/S nomenclature for the allenes:

1. Viewing of molecule from left side



2. Viewing of allene from Right side



2.9 Representation of Enantiomers of the allenes

The enantiomer of allenes can represents in following ways. Mirror image of the allenes is shown in figure 7. The compound I and its enantiomers can be written if one terminal carbon atom substituent is interchanged. Compound I, right terminal carbon atom substituents interchanging gives its enantiomer II and If compound I left carbon atom substituent interchanging will give its enantiomer III (Figure 7).

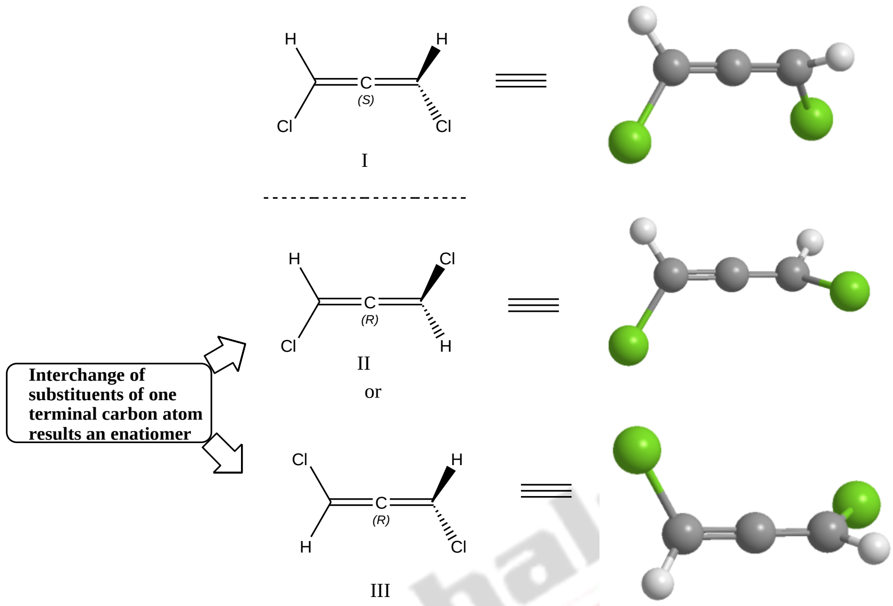


Fig. 7: Mirror images of allenes (representation of both enantiomers)

These three compounds are written above, their enantiomers are identify by giving the absolute configuration according the viewing through axis.

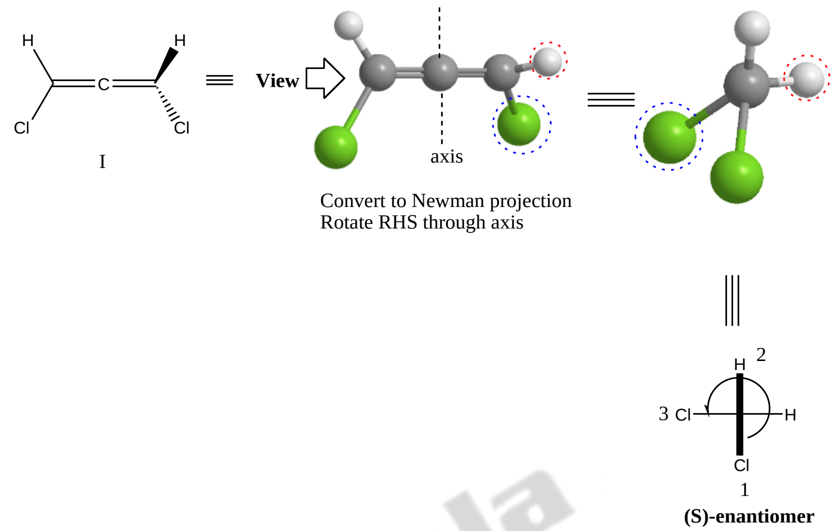


Fig. 8: Absolute configuration (S)-enantiomer

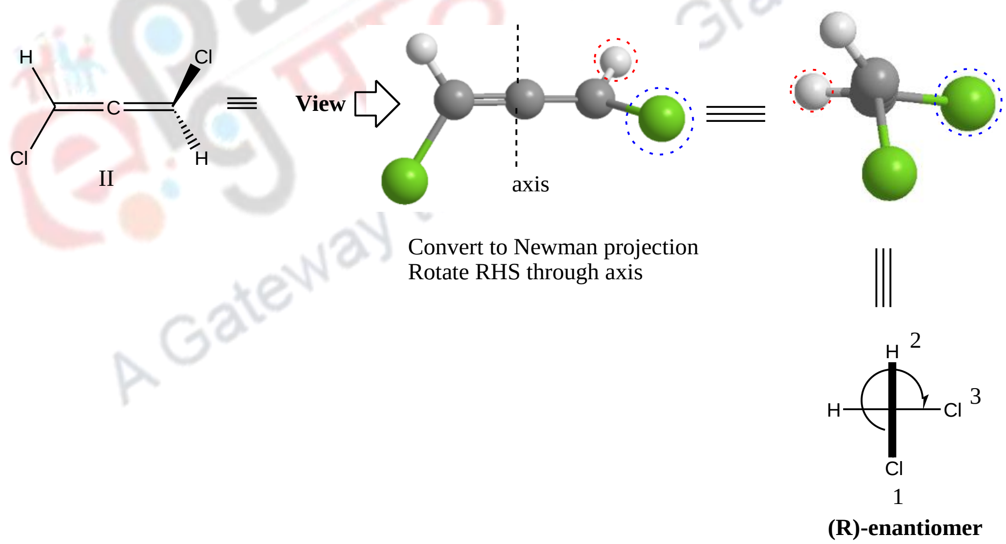


Fig. 9: Absolute configuration (*R*)-enantiomer

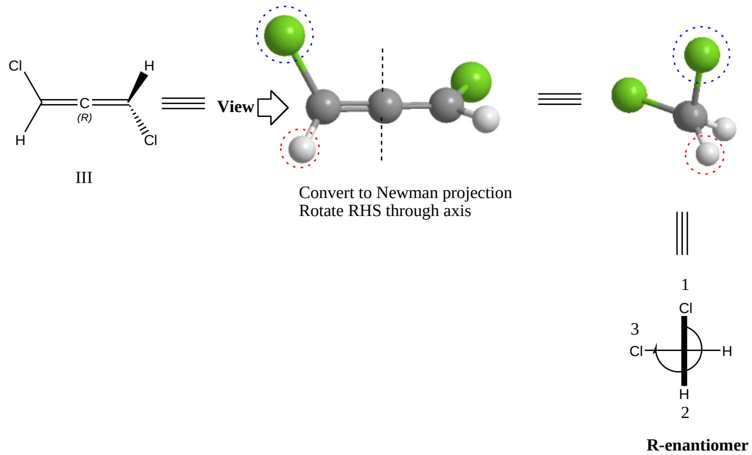


Fig.10: Absolute configuration (*R*)-enantiomer

3. Summary

- This module will give the understanding of the stereoisomerism of allene and three dimensional structure of the allene.
- Allenes are the examples of axial chirality. Allenes central carbon is sp hybridized and terminal carbon atoms are sp^2 hybridized.
- Allenes moiety also exists in many natural products.