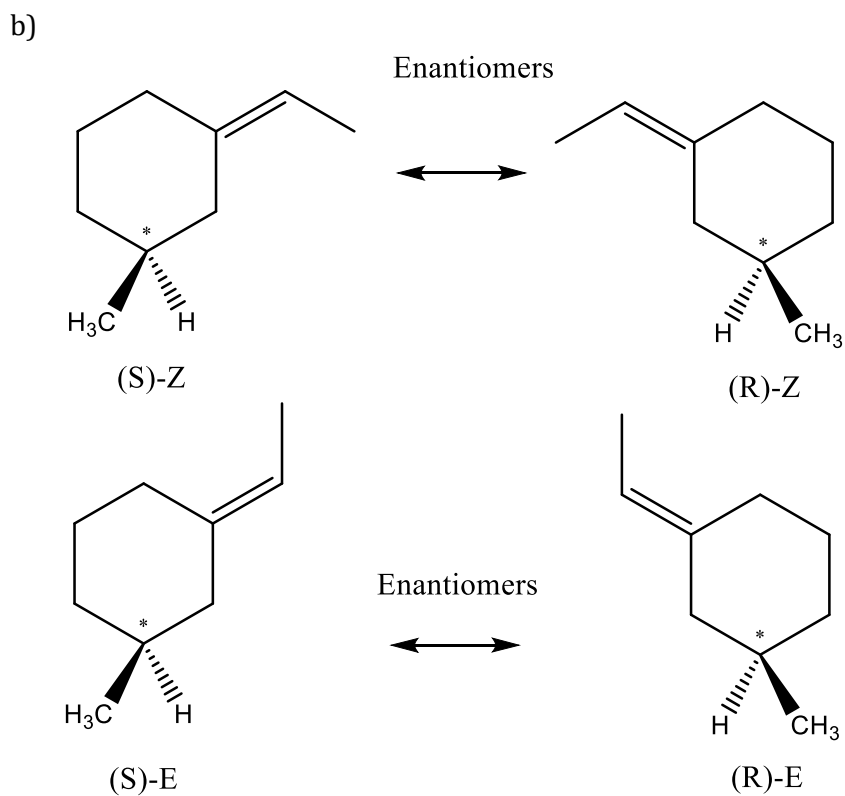
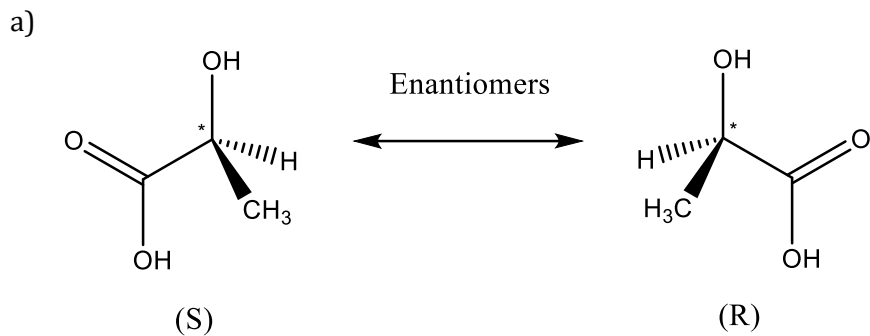
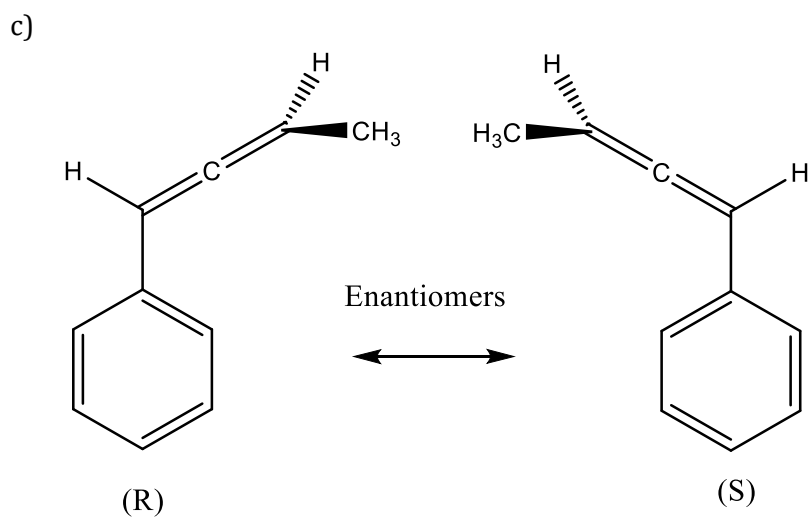
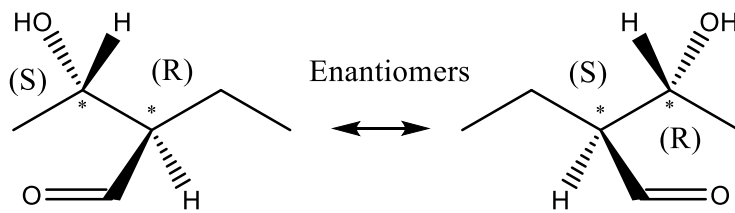
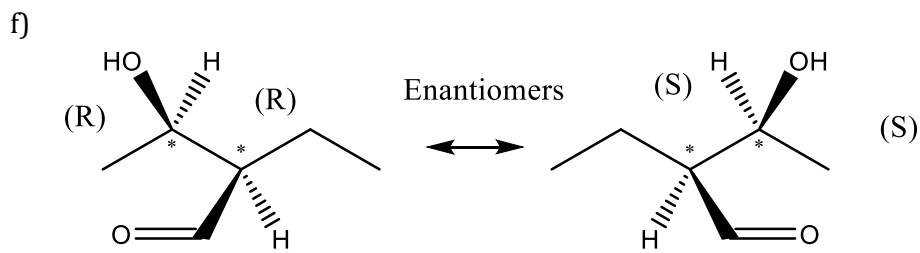
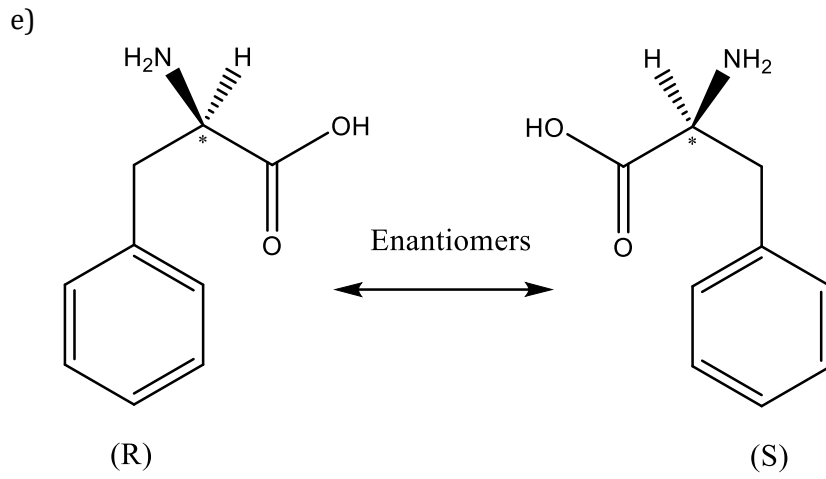
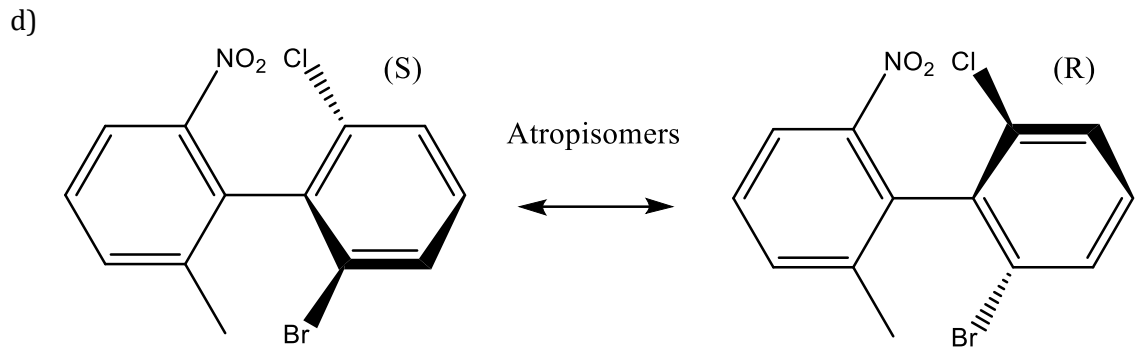


1.

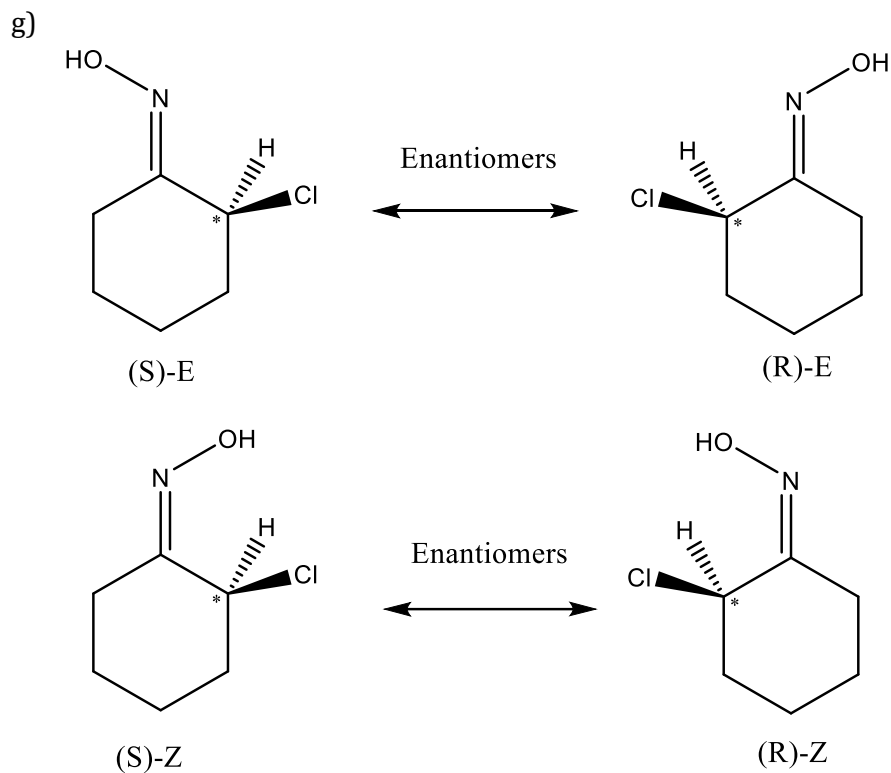


All other pairs are diastereomers.

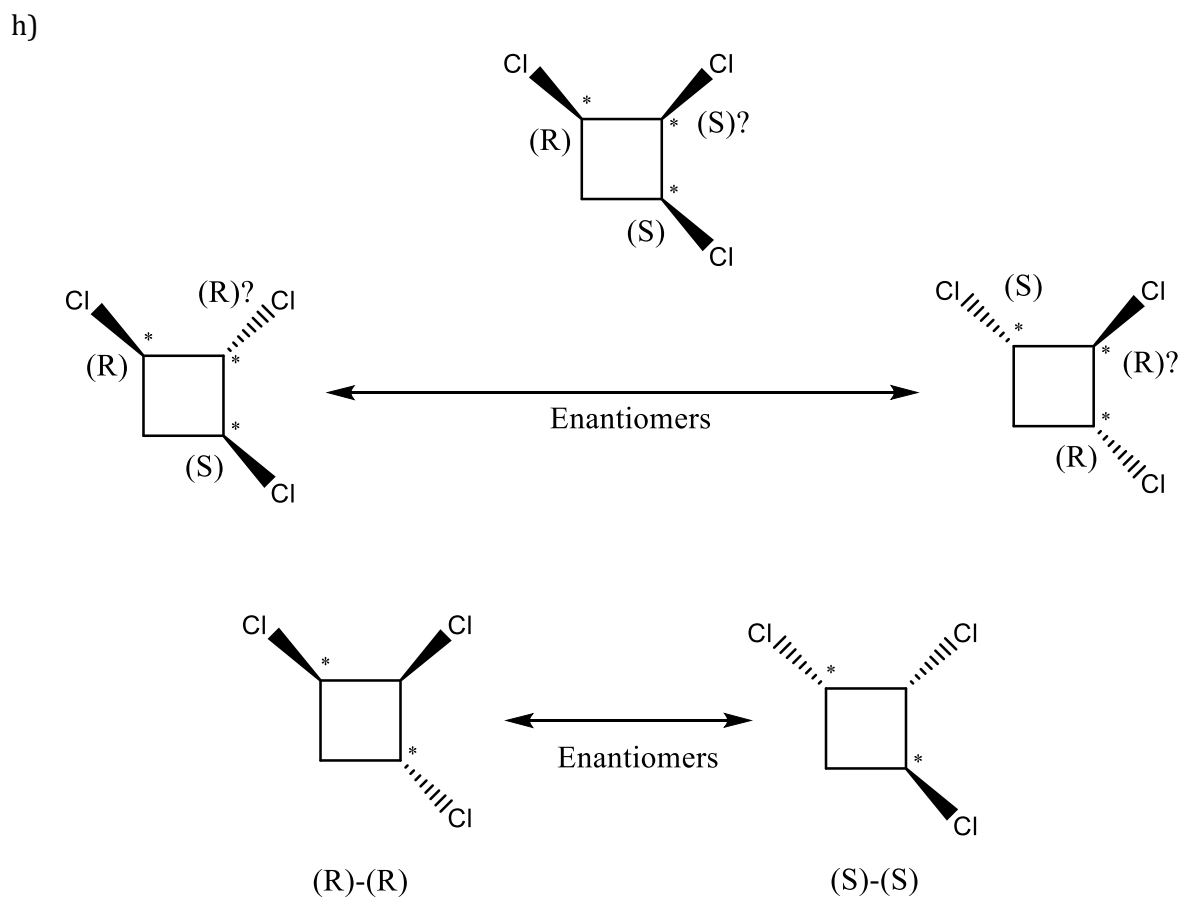




All other pairs are diastereomers.



All other pairs are diastereomers.



All other pairs are diastereomers.

2.

Cahn-Ingold-Prelog nomenclature is a system of rules to assign priority to the substituents on chiral centres and double bonds so that any molecule can be uniquely described using R/S and E/Z labels.

For chiral centres and double bonds, each substituent is given a priority based in its mass.

- i) For each atom bonded directly to the carbon atom, order them based on atomic number. Atoms with larger atomic number have higher priority.
- ii) If two atoms have the same atomic number, the next atom in the chain is considered. This process is continued until there is a difference.
- iii) If the only difference between two groups is the isotopes, the atom with the larger atomic mass is assigned priority.
- iv) If the substituents contain double bonds or triple bonds, each double or triple bond is replaced by either two or three singly-bonded duplicates of the atoms on the other end of the double or triple bond.
- v) If the two substituents differ only in the arrangement of a double bond, the Z isomer takes priority over the E isomer.
- vi) Cyclic molecules are treated as a tree. Once an atom has been reached that is already in the tree, the chain is terminated.

Once priority has been assigned to each substituent, a label can be applied to the chiral centre.

For chiral centres, the substituent with the lowest priority is directed into the plane, while the other three substituents are considered. If the substituents descend in priority while considering them clockwise, the label R is assigned. If the substituents descend in priority while considering them anticlockwise, the label S is assigned.

For this example, the chiral centre first must be identified. Then the substituents are given priority.

- i) There are three carbons and one hydrogen directly bonded to the chiral carbon, so the hydrogen is given lowest priority, which in this case is 4.
- ii) The next atom in the chain is considered. The phenyl ring is directly bonded to two carbon atoms (plus one phantom carbon atom) whereas the other two groups are both bonded to oxygen atoms, hence the phenyl substituent is the next lowest in priority and is assigned a value of 3.
- iii) Next, the two substituents with the oxygens are considered. The alcohol substituent has one oxygen and two hydrogens whereas the carbonyl substituent has one oxygen, one carbon and a phantom oxygen atom, which takes priority as oxygen takes priority over hydrogen. Hence the alcohol is assigned the label 2 and the carbonyl substituent 1.

Now the molecule must be projected with the hydrogen atom directed away from the observer. Now the substituents are considered in clockwise fashion: If they proceed in the order 1, 2, 3, the label R is assigned. Otherwise, the label S is assigned.

3.

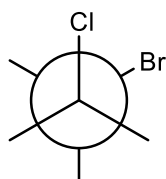
On each atom of a double bond, the two substituents can be ordered based on their priority in a similar fashion, with one being higher in priority than the other. For the entire double bond, if two substituents of higher priority are on the same side, the label Z is assigned. For double bonds where the two substituents of higher priority are on the opposite side, the label E is given.

In this example of an alkene, the substituents are given priority:

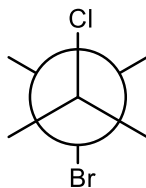
- i) On the carbon of the double bond which is bonded to chlorine and an ethyl chain, the chlorine takes priority as it is higher its atomic number than the carbon of the ethyl chain.
- ii) On the other carbon of the double bond, the bromine takes priority over the formyl group.

The bromine and chlorine are on the same side of the double bond, hence the label Z is assigned.

4.



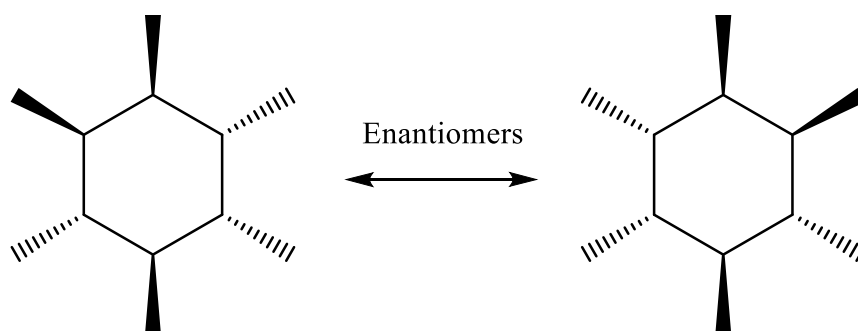
Gauche conformation



Antiperiplanar conformation

The gauche conformation is chiral as it cannot be superimposed in its mirror image.

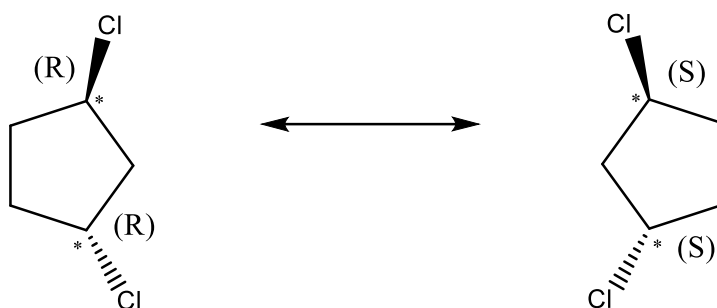
5.



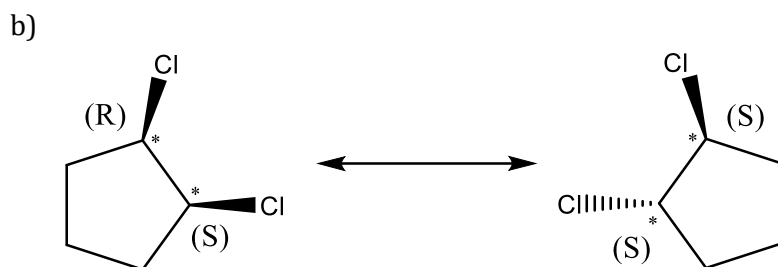
6.



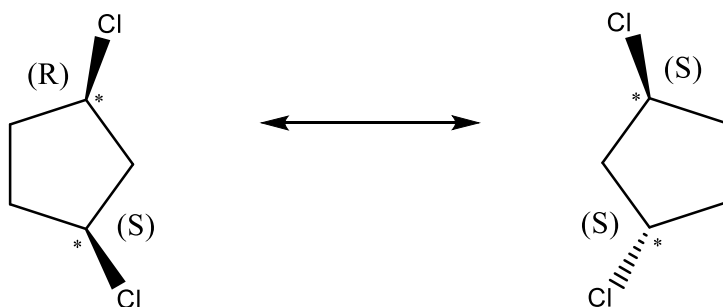
Enantiomers



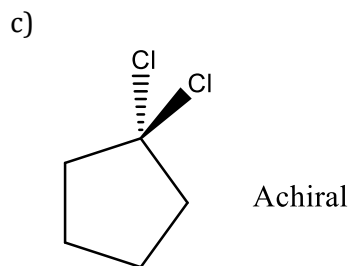
Enantiomers are pairs of molecules which are mirror images of one another but are not superimposable on one another. They most often come about due to the presence of one or more chiral centres in the molecule.



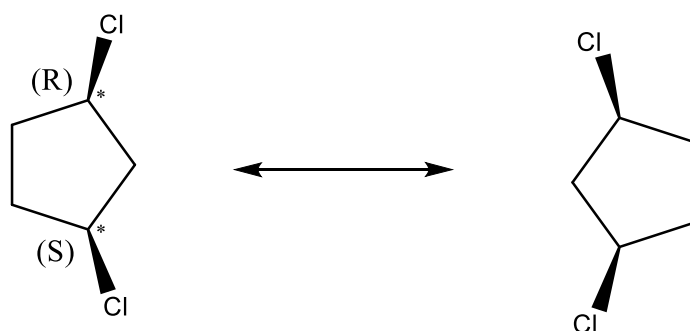
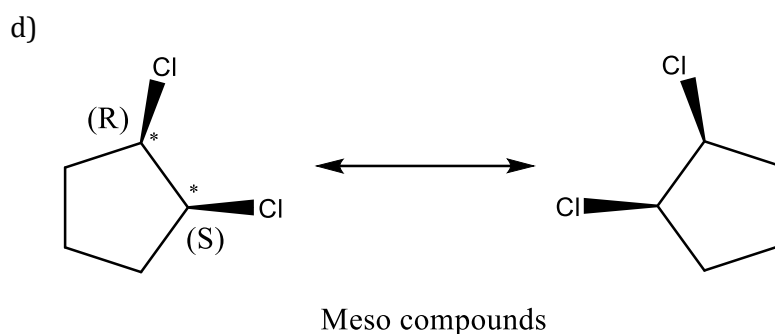
Diastereomers



Two molecules are said to be diastereomers if they are not superimposable yet are also not mirror images of each other. If two diastereomers differ by the configuration of only a single carbon centre, they are said to be epimers.



An achiral molecule does not contain any chiral centres. In this case, every carbon atom is bonded to either two chlorine atoms or two hydrogen atoms, hence there are no chiral carbons.



Meso compounds are molecules which contain chiral centres yet are superimposable on their mirror images.

e)  
A racemic mixture or racemate is a mixture containing equal amounts of a pair of enantiomers. Racemic mixtures do not rotate plane-polarised light, as the isomers are present in equal amounts.

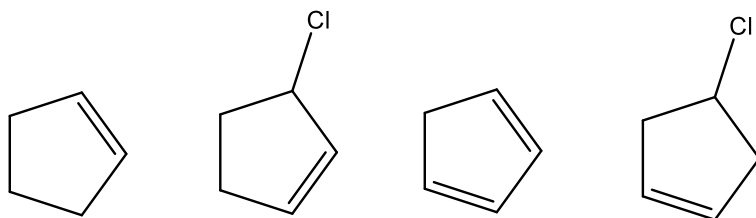
f)  
Optical activity refers to the property of a compound in which plane-polarised light is rotated. Enantiopure mixtures are optically active.

g)  
The prefix *gem-* refers to an abbreviation of geminal, which means that two functional groups are substituents of the same atom. If the substituents are on adjacent atoms, they are said to be vicinal.

h)

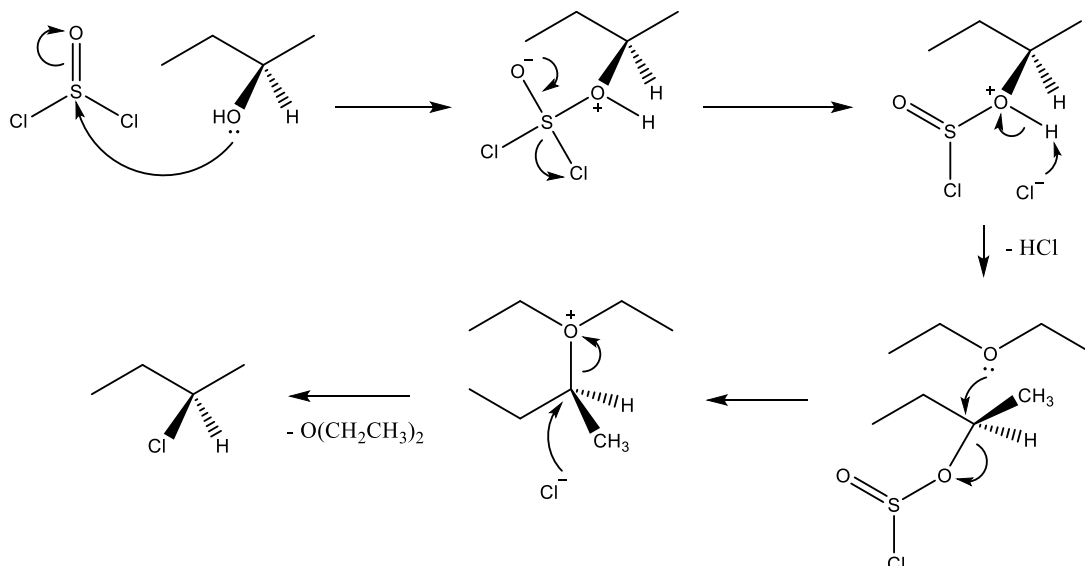
Eclipsed refers to a conformer in which the bonds of the two atoms on a sigma bond are in line with each other when viewed down the axis of the bond. In other words, the dihedral angle is zero. These conformers are high in energy in comparison to the staggered conformation.

Elimination products:



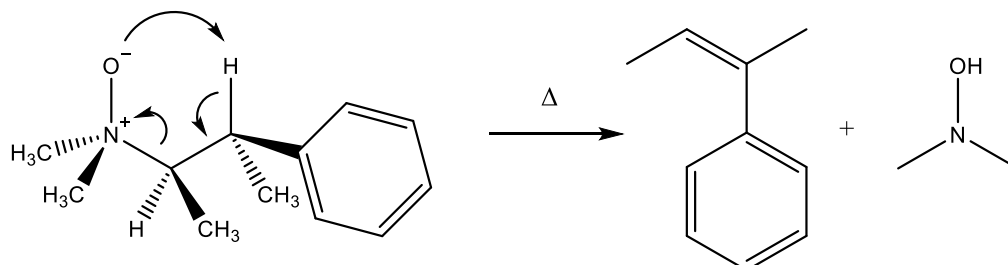
7.

a)



Reaction proceeds through two successive  $S_N2$  reactions hence there is a retention of stereochemistry. No intimate ion pair forms due to the nucleophilicity of the solvent.

b)

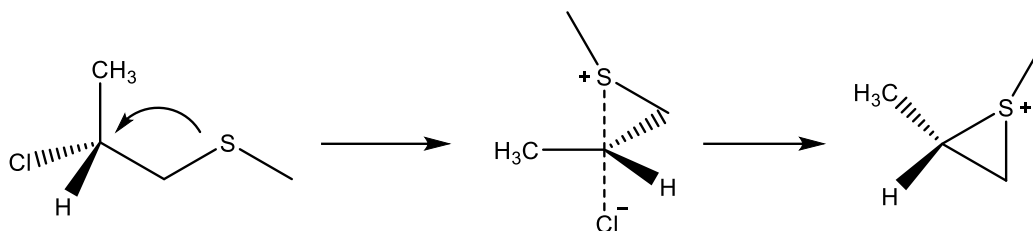


Heat causes an intramolecular elimination reaction where the oxide ion acts as a base. The formation of a 5-membered transition state means that the hydrogen and nitrogen must be syn, which leads to the formation of the Z isomer.

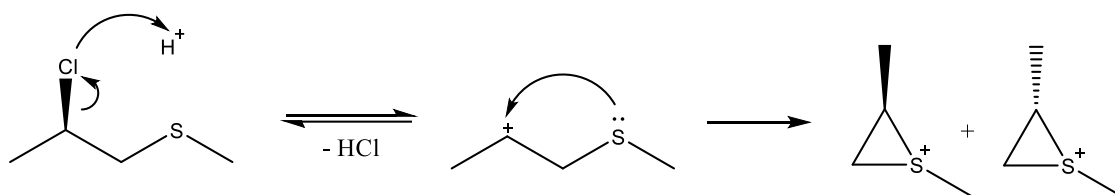


c)

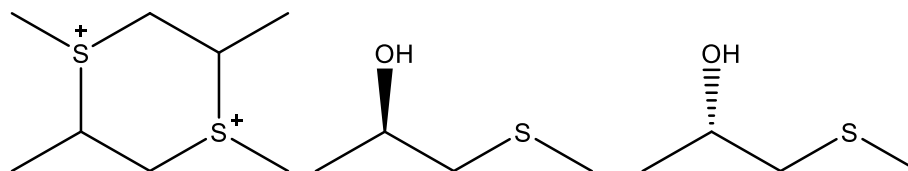
Here, the carbon undergoes nucleophilic attack and the chlorine is displaced.



One possible mechanism is through a single step  $S_N2$  reaction with an inversion of stereochemistry where the sulphur acts as a nucleophile.



Another possible mechanism is through an  $S_N1$  mechanism where the solvent facilitates the dissociation of the alkyl chloride into a carbocation. This results in a mixture of stereoisomers. This reaction is more likely due to the protic nature of the solvent, which stabilises the ion and the product.



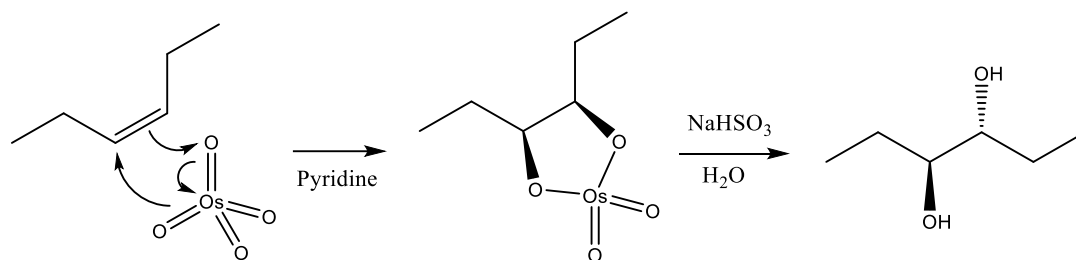
Due to the strained nature of the 3-membered ring, it's possible that the molecule will dimerise, although intramolecular reactions are kinetically favoured.

Another possibility is the simple hydrolysis of the alkyl chloride to form an alcohol with a mixture of both isomers.

The overall most probable is the intramolecular  $S_N1$  reaction.

8.

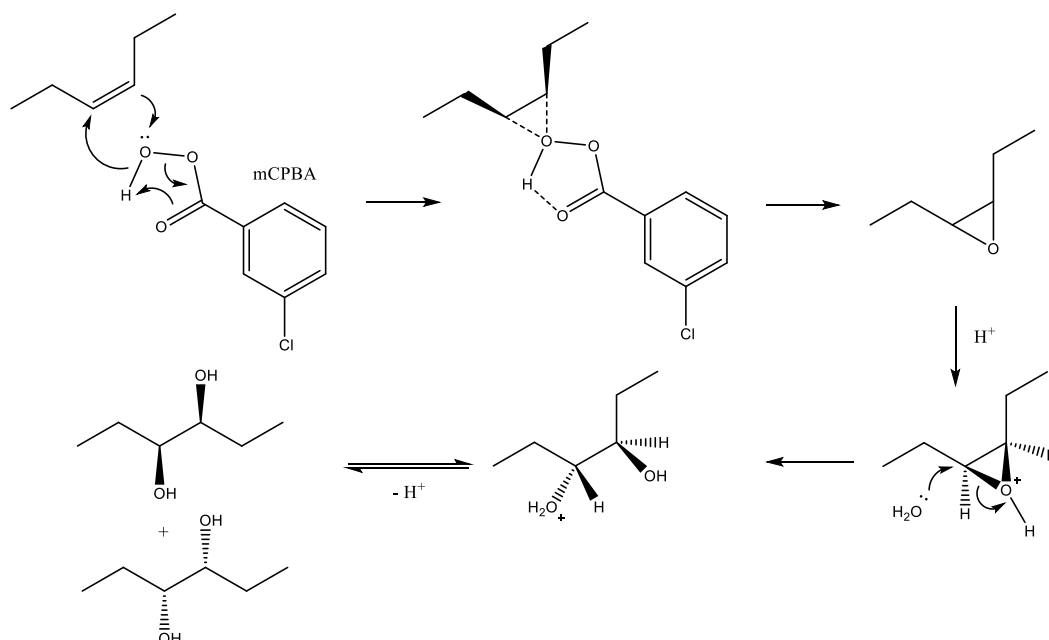
a)



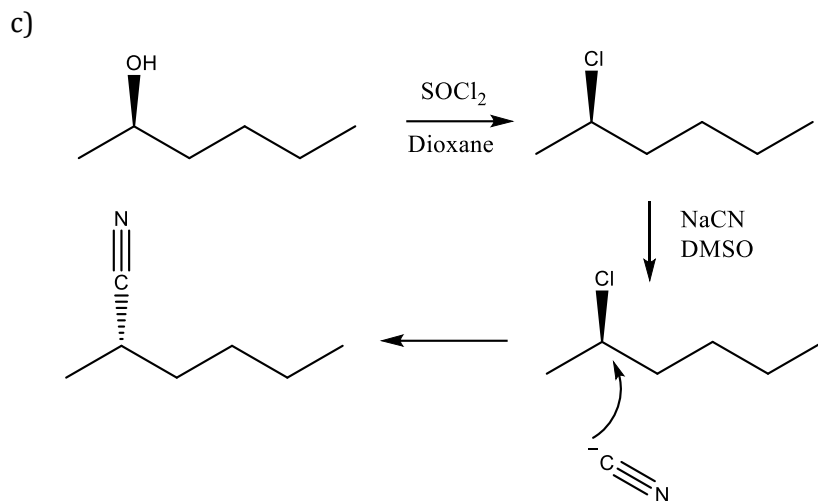
Here, osmium tetroxide hydroxylates the double bond twice in a single step to form a vicinal diol in syn arrangement. The Z isomer of the double bonded compound produces the meso compound.

The workup involves using sodium bisulfite to break down the osmium complex.

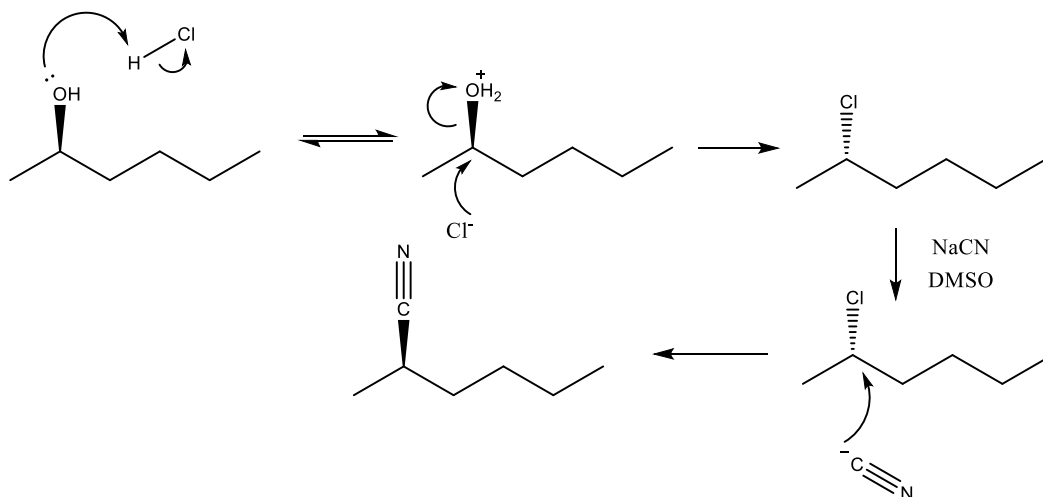
b)



Here, the cis alkene is first epoxidated and subsequently hydrolysed with acid to form a vicinal diol in the anti-configuration. As the mCPBA can attack from either above or below the double bond, a racemate is formed.



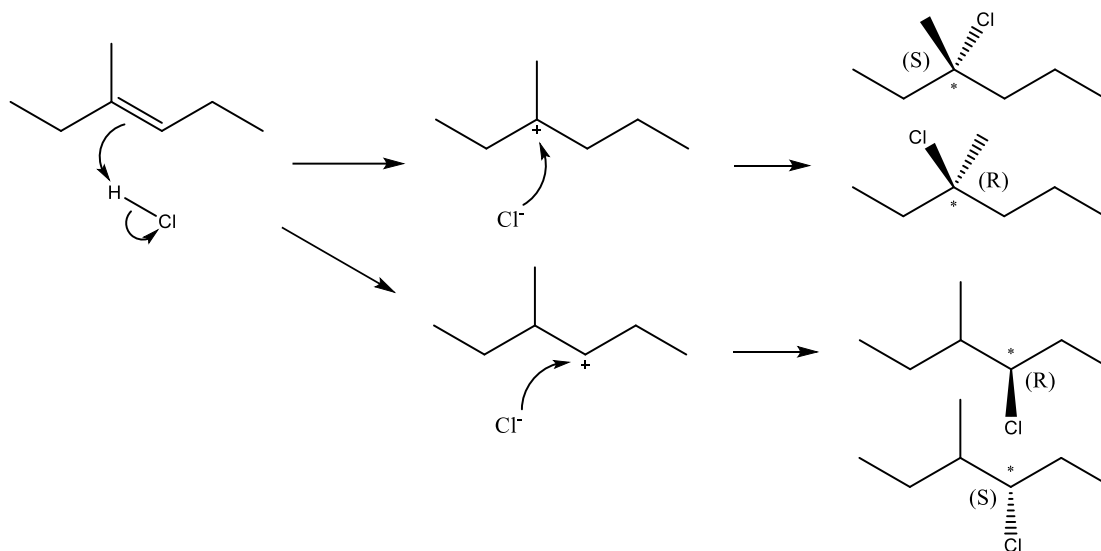
The first reaction produces the alkyl chloride with retention of stereochemistry so that an  $\text{S}_{\text{N}}2$  attack of the cyanide will produce the S enantiomer. DMSO is used to suppress the formation of the isonitrile, which can be removed with acid in the work up.



Two  $\text{S}_{\text{N}}2$  reactions occur in succession which results in retention of stereochemistry and forms the R enantiomer.

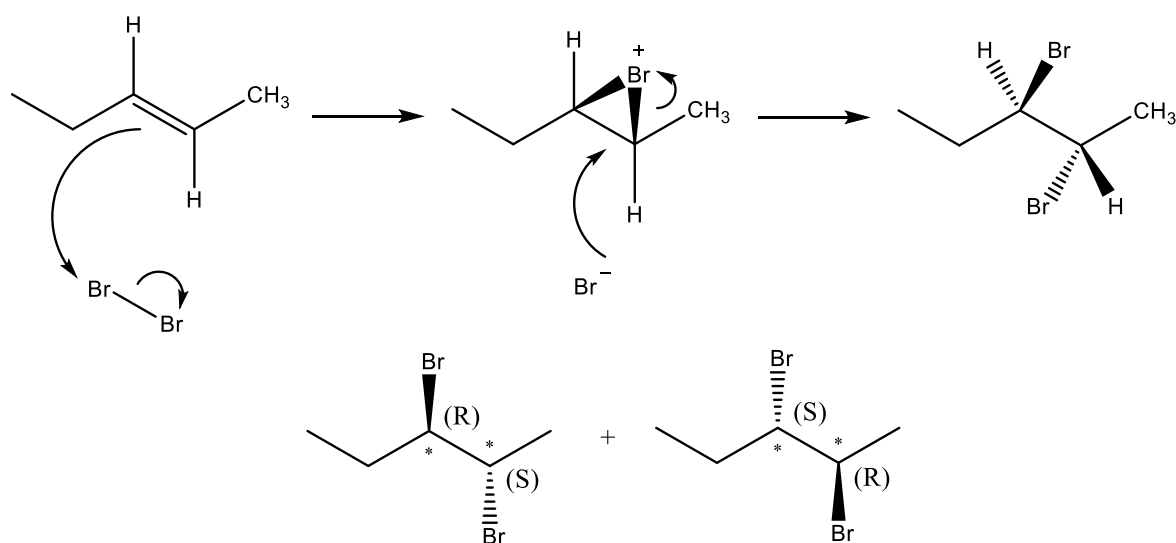
9.

a)



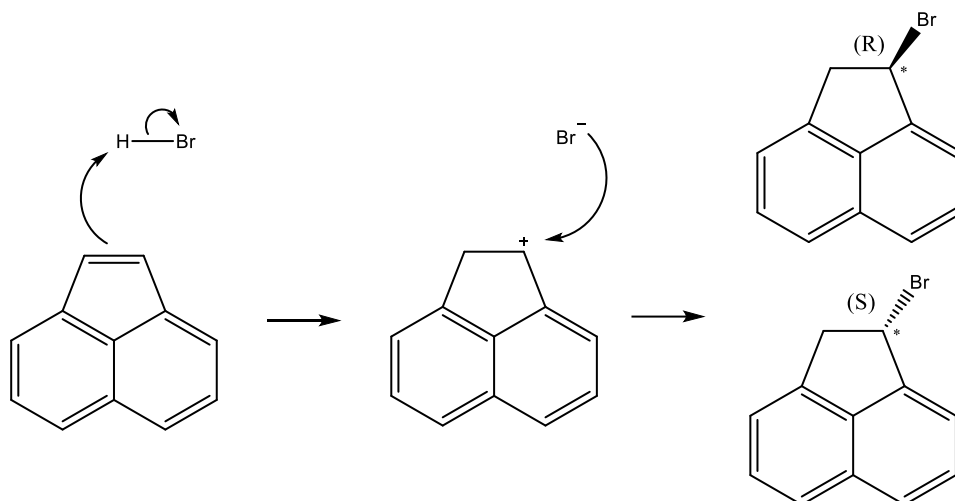
Here, the Markovnikov product is favoured. This mechanism involves the formation of a carbocation which is  $sp^2$  hybridised and the chloride can attack from either above or below the plane. In either case, a racemate is formed.

b)

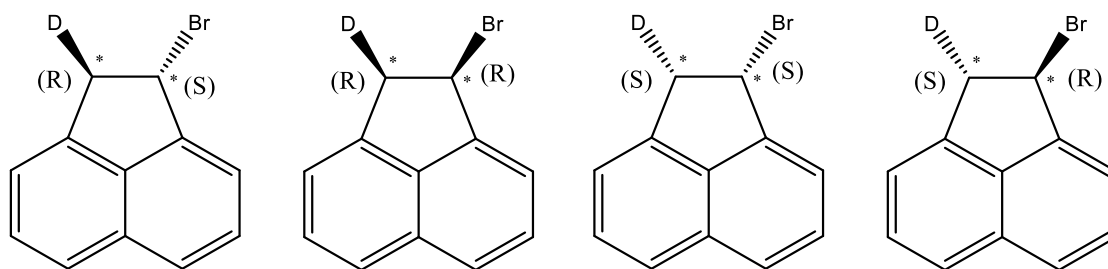


The formation of a brominium ion means that the bromide adds anti to the original bromine. Because both configurations of alkyl groups (two ethyls vs one propyl and one methyl) have similar stabilising ability of the cation, both enantiomers form.

c)



The carbocation is sp<sup>2</sup> hybridised which means the bromide can attack above or below the plane, resulting in a racemic mixture. The symmetry of the naphthalene ring means that two pairs of isomers are equivalent.



If a deuterated form of hydrogen bromide is used, two stereocenters are formed which results in four optical isomers which consists of two pairs of enantiomers.