

Isomerism

It is possible for organic molecules with the same molecular formula to have different structures

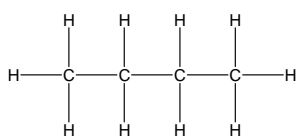
Definition- Structural isomers: same molecular formula different structures (or structural formulae)

There are three types of structural isomerism

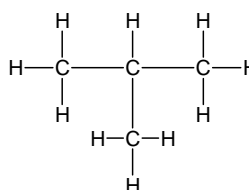
- Chain isomerism
- Position isomerism
- Functional group isomerism

Chain isomerism: Compounds with the same molecular formula but different structures of the carbon skeleton

These isomers arise because the carbon chains can be branched. For example, there are two isomers of butane, C_4H_{10} . In one of them, the carbon atoms lie in a "straight chain" whereas in the other the chain is branched

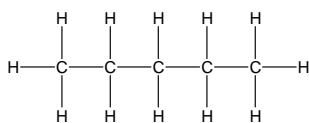


butane

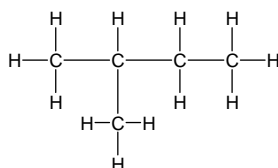


methyl propane

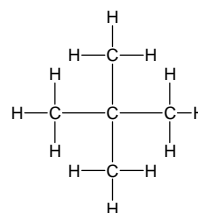
There are three isomers of pentane C_5H_{12}



pentane



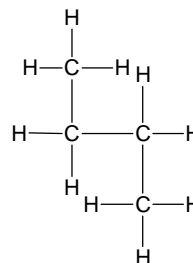
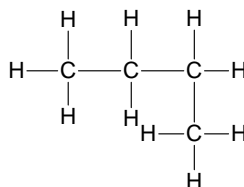
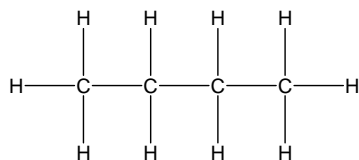
2-methylbutane



2,2-dimethylpropane

False isomers

Do not draw "false" isomers which are just twisted versions of the original molecule. Twisting the molecule into a different shape does not make a different isomer. Isomers are only formed if a bond would have to be broken and reassembled into the different structure

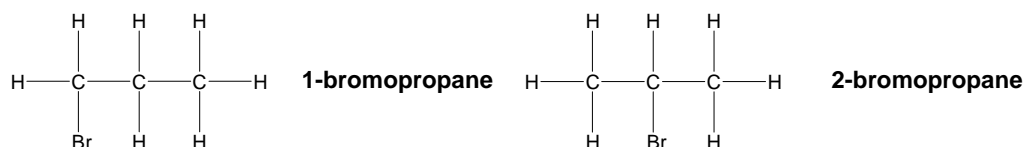


These are all exactly the same compound.

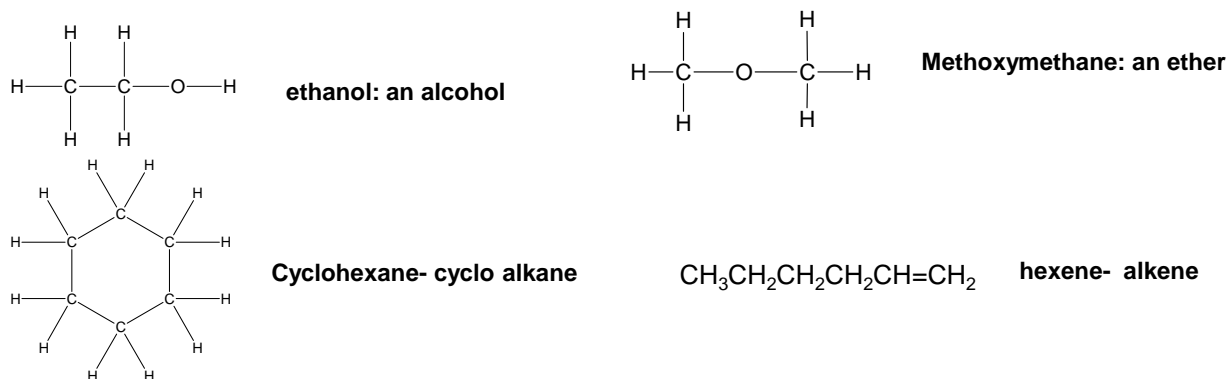
Number of Possible Chain Isomers for Selected Alkanes

Molecular Formula	Number of possible isomers
C_4H_{10}	2
C_5H_{12}	3
C_6H_{14}	5
C_7H_{16}	9
C_8H_{18}	18
C_9H_{20}	35
$C_{10}H_{22}$	75
$C_{15}H_{32}$	4,347
$C_{20}H_{42}$	336,319
$C_{30}H_{62}$	4,111,846,763

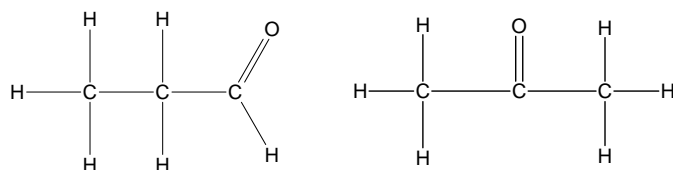
Position isomers: Compounds with the same molecular formula but different structures due to different positions of the same functional group on the same carbon skeleton



Functional group isomers: Compounds with the same molecular formula but with atoms arranged to give different functional groups



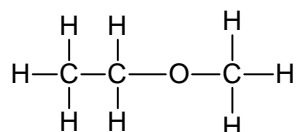
Aldehydes and ketones of the same chain length would be classed as functional group isomers- e.g. Propanal and propanone (both C_3H_6O)



Structural Isomer Questions

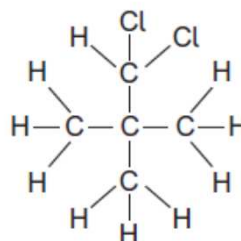
- 1) a) Define what a structural isomer is.
b) Define what a molecular formula is.
- 2) Draw all the structural isomers of hexane and name them. What type of structural isomers are these isomers?
- 3) a) Draw the displayed formulae and name all the straight-chain isomers with the molecular formula $C_4H_8Br_2$
b) Name the type of structural isomerism that these isomers show and explain why
- 4) a) Name and draw the displayed and skeletal formulae of a functional group isomer of pent -1-ene
b) Name and draw the displayed and skeletal formulae of a positional isomer of pent -1-ene
c) Name and draw the displayed and skeletal formulae of a chain isomer of pent -1-ene

5) The following is the structure of methoxyethane

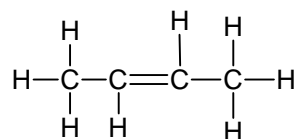


- a) Draw the displayed formulae and name a functional group isomer of methoxyethane
 - b) Draw the displayed formulae and name a positional isomer of the compound you have drawn in part 5a
- 6) Draw the skeletal formulas of the structural isomers of the different alcohols with the molecular formula $C_4H_{10}O$. Name the isomers.
- 7) Deduce the number of structural isomers for Hexane C_6H_{14}

8) Name the compound on the right and draw its skeletal formula. Deduce how many **other** position isomers of the compound on the right can be formed.



9) Compound **Y** is shown below. It is a member of a homologous series of hydrocarbons.

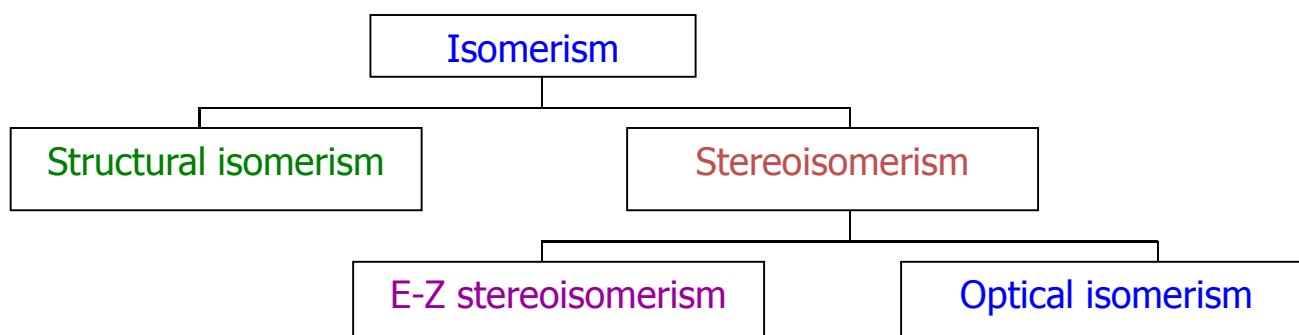


- (a) Write the general formula of the homologous series that contains **Y**.
- (b) Name a process used to obtain a sample of **Y** from a mixture containing other members of the same homologous series.
- (c) Name and draw the skeletal formula of a position isomer of **Y**.
- (d) Name and draw the skeletal formula of a functional group isomer of **Y**.

Stereoisomerism

Definition: Stereoisomers have the same structural formulae but have a different spatial arrangement of atoms

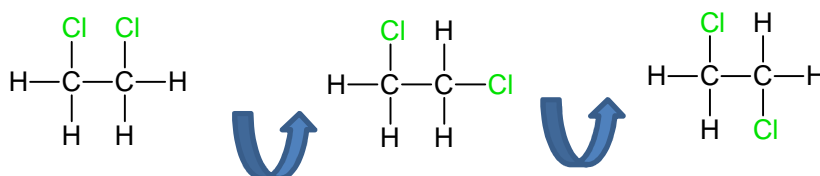
There are two types of **stereoisomerism**: geometrical (E- Z isomerism) and optical isomerism



E-Z stereoisomerism

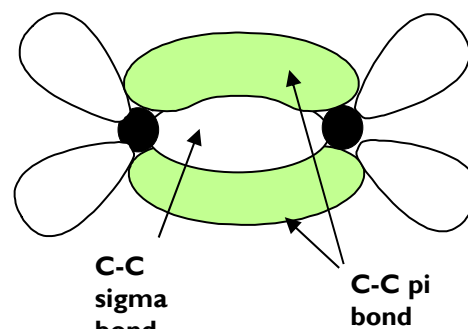
Alkenes can exhibit a type of isomerism called **E-Z stereoisomerism**. This occurs because of restricted rotation that occurs around a double bond

Single carbon-carbon covalent bonds can easily rotate



All three of these structures are the same

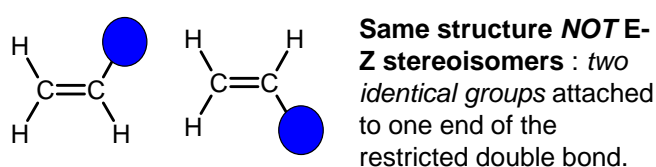
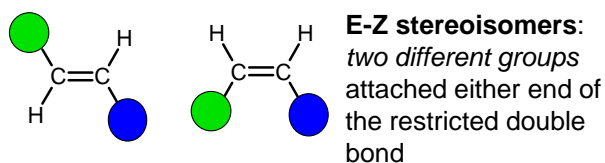
C=C double bonds have restricted rotation, due to position of the pi bond, so the groups on either end of the bond are fixed in one position. It is not easy to flip between the two.

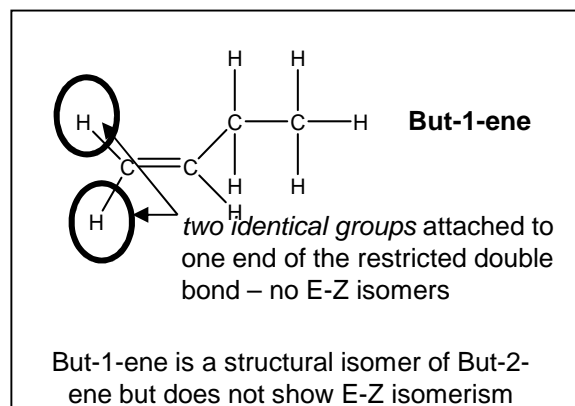
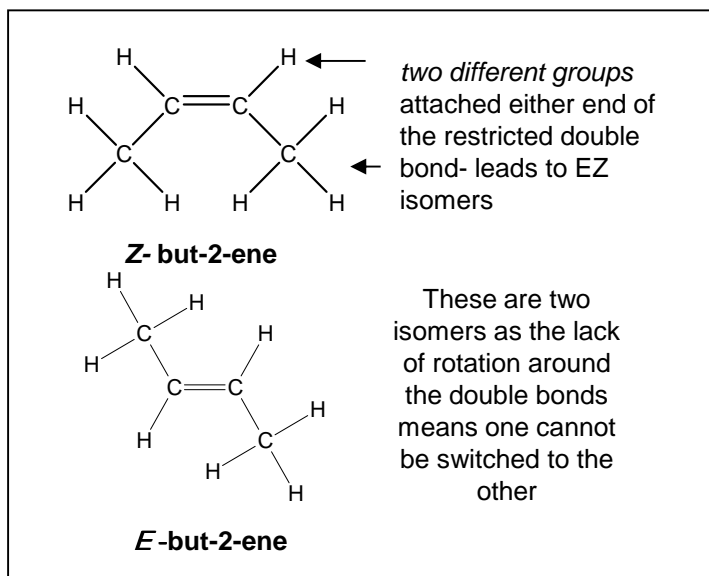


This produces two possibilities. The two structures cannot interchange easily so the atoms in the two molecules occupy different positions in space.

E-Z stereoisomers arise when:

- There is **restricted rotation** around the C=C double bond.
- There are **two different groups/atoms** attached both ends of the restricted double bond



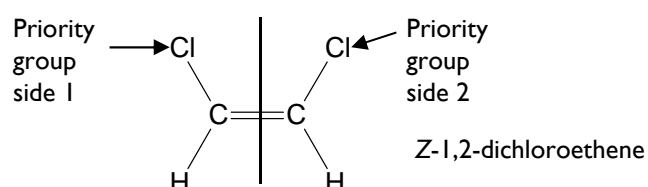
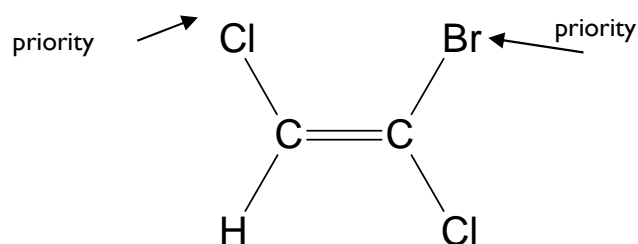


Naming E-Z stereoisomers

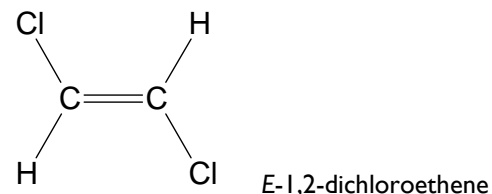
Cahn–Ingold–Prelog (CIP) priority rules.

On both sides of the double bond determine the priority group

1. Compare the atomic number (A_r) of the atoms directly attached to each side of the double bond; the group having the atom of higher atomic number receives higher priority.

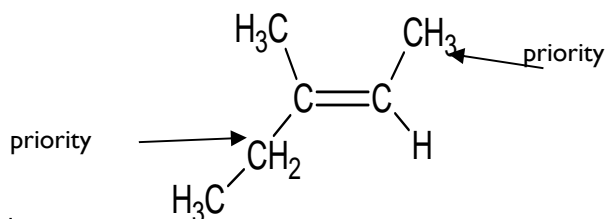


If the priority atom is on the same side of the double bond it is labelled Z from the german zusammen (The Zame Zide!)



If the priority atom is on the opposite side of the double bond it is labelled E from the german entgegen (The Epposite side!)

2. If there are groups of atoms instead of single atoms attached to the carbon of the double bond then consider the sum of the atomic numbers of the entire group. The bigger group is the priority

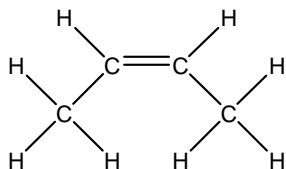


The CH_3CH_2 group is bigger than the CH_3 so it is the priority group

cis-trans isomerism

In some text books you will find this type of E-Z isomerism referred to as geometric isomerism and cis-trans isomerism.

cis-trans isomerism can be considered as a special case of *E/Z* isomerism in which two of the substituent groups are the same. It has been superseded by *E/Z* isomerism because the **Cahn-Ingold-Prelog (CIP) priority rules** allow all alkenes to be considered and not just the ones where the groups are the same .

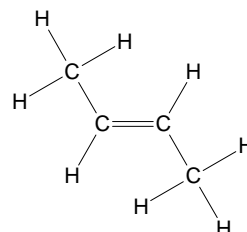


Z- but-2-ene

Can also be called

Cis- but-2-ene

Cis means "on this side of" in latin



E- but-2-ene

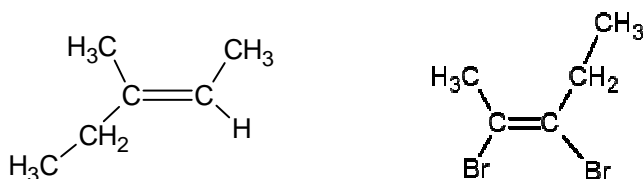
Can also be called

trans- but-2-ene

trans means "across" in latin

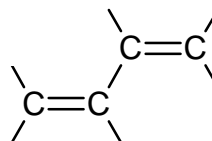
E-Z Isomerism Questions

1. State the meaning of the term *stereoisomers*
2. Identify the feature of the double bond in but-2-ene that causes it to form two EZ stereoisomers
3. Draw structural formulae of the E-Z isomers of the following compounds
 - a) 3-methylpent-2-ene.
 - b) but-2-ene
 - c) 3-methylpent-2-ene
 - d) pent-3-en-2-ol
 - e) hex-3-ene
 - f) pent-2-ene
4. Name the following including the correct E-Z letter at the start of the name

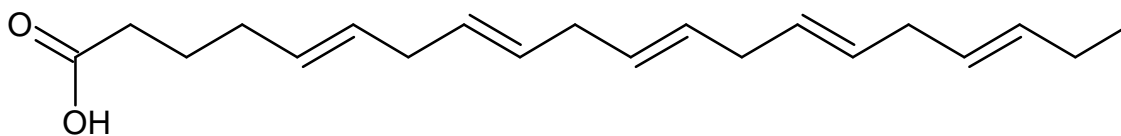


5. Compound A has the molecular formula $C_5H_{10}O$. It has a branched carbon chain and exists as a pair of E-Z Stereoisomers. Draw the structures and name the two Isomers.

- 6 Using the carbon skeleton like it is drawn on the right, Draw the 3 stereoisomers of 1,4-dichlorobuta-1,3-diene.

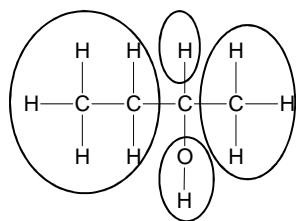


7. Draw the two E-Z stereoisomers of hex-4-en-2-one.
8. Explain why the following weak unsaturated acid $CH_3(CH_2)_4COOH$ shows EZ isomerism. Draw the structures of each of the E-Z isomers of this acid.
9. How many E-Z stereoisomers are there of the molecule shown below, including the molecule shown?



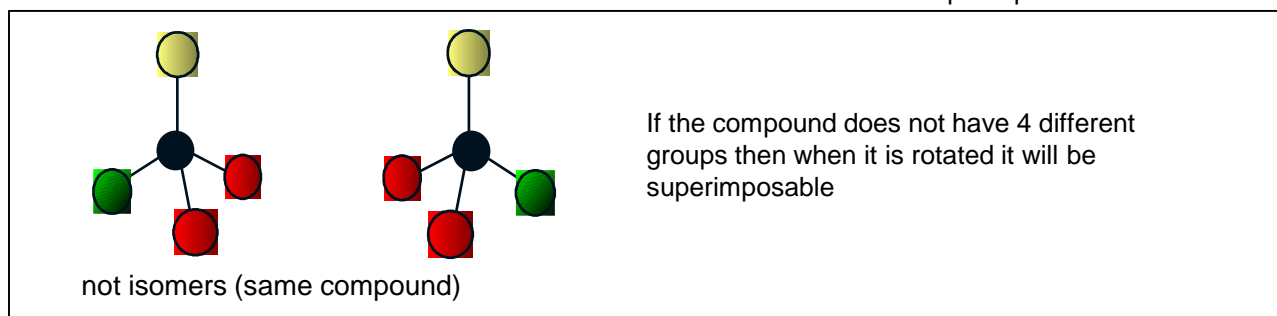
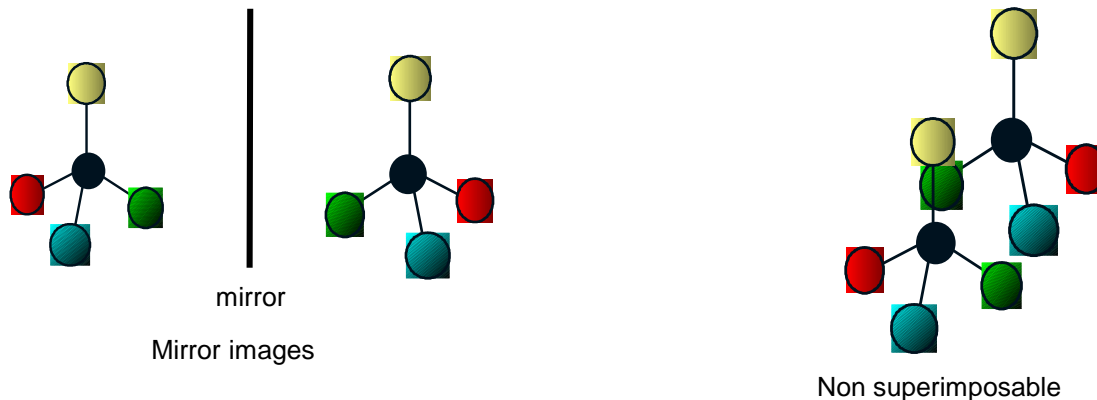
Optical Isomerism

Optical isomerism occurs in carbon compounds with 4 different groups of atoms attached to a carbon (called an **asymmetric carbon**).

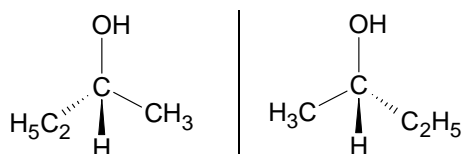


A carbon atom that has four different groups attached is called a **chiral** (asymmetric) carbon atom

This causes two different isomers that are not superimposable to be formed. They are mirror images



Butan-2-ol has four different groups around a carbon and so forms optical isomers

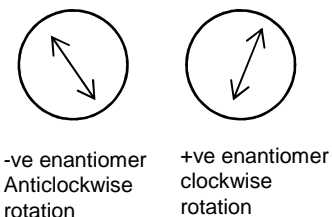


Two compounds that are optical isomers of each other are called **enantiomers**.

Optical isomers have similar physical and chemical properties, but they rotate plane polarised light in different directions.

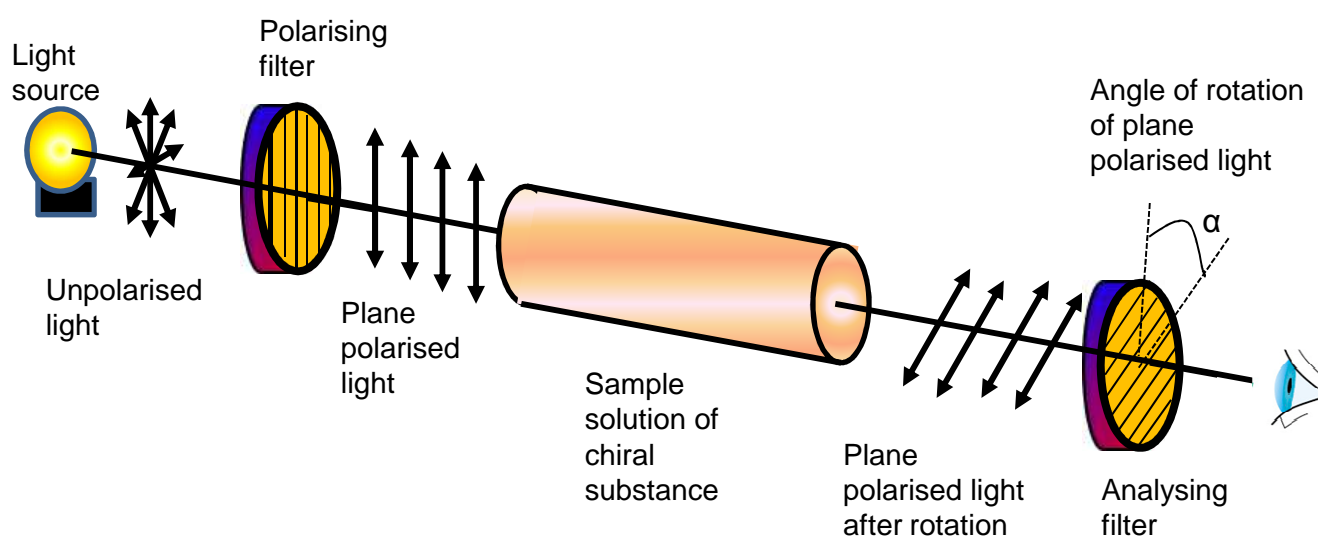
One enantiomer rotates it in one direction and the other enantiomer rotates it by **the same amount in the opposite direction**.

One optical isomer will rotate light clockwise (+)(called dextrorotatory).
The other will rotate it anticlockwise(-)(called laevorotatory).



Polarimeter

The rotation of light by a chiral compound can be observed by using a polarimeter. The light source will produce unpolarised light which is light travelling in all planes. If this light is passed through a polarising filter then plane polarised light will be formed, which is light that only travels in one plane. When this passes through the sample of the chiral substance the plane polarised light will rotated in to a different plane.



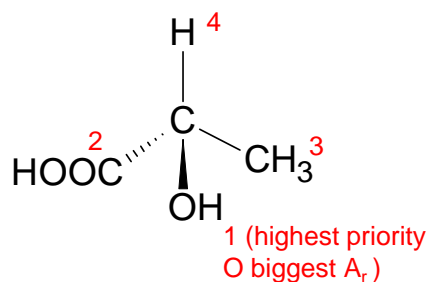
Method for using a polarimeter

- first put water in sample tube and rotate analysing filter to block out light
- replace water with sample. If the sample is chiral light will be seen
- rotate analysing filter again to block out light. The amount the analyser is rotated is the amount the light has been rotated.

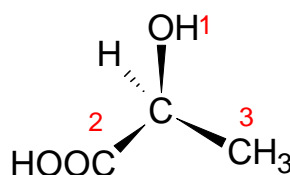
R/S Nomenclature

Different systems of nomenclature are in existence for optical isomers. D/L or +/- are commonly used, but both have been superseded by the more informative R/S system.

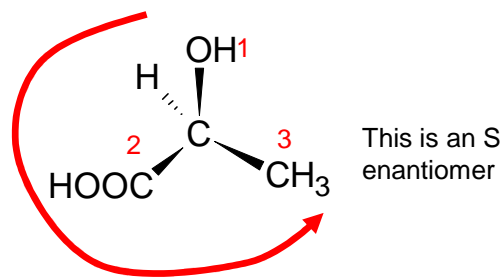
1) Using the Cahn–Ingold–Prelog (CIP) priority rules, used in E/Z isomerism, assign a priority number for each of the four groups. The ones with the higher atomic number A_r have the higher priority.



2) Redraw the molecule with the atom with the lowest priority pointing into the plane of the page (in this case H)



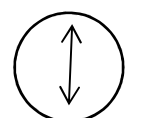
3) Imagine moving from substituent 1 to 2 to 3. If moving in a clockwise direction then assign the compound the R letter. If moving anticlockwise then assign the compound the S letter



Racemic mixtures

A mixture containing a 50/50 mixture of the two isomers (enantiomers) is described as being a **racemate** or **racemic mixture**.

A racemic mixture (a mixture of equal amounts of the two optical isomers) **will not rotate** plane-polarised light.

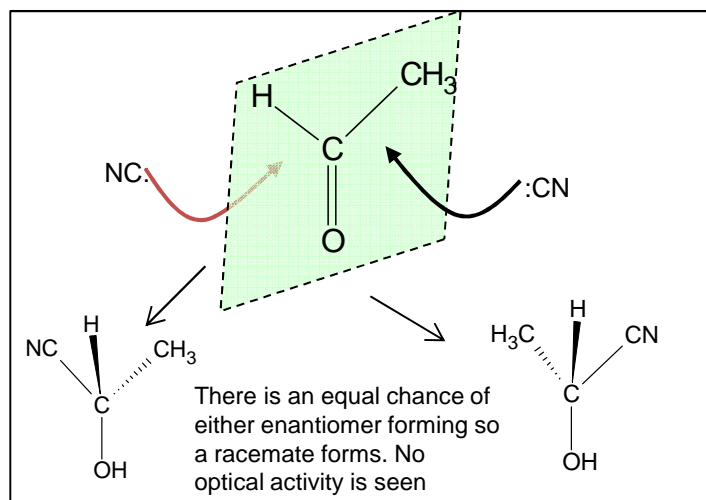


Racemate
no rotation

Chemical Reactions and Optical Isomers

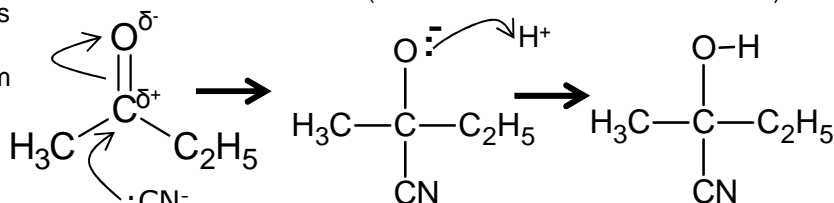
Formation of a racemate

A racemate will be formed in a reaction mechanism when a trigonal planar reactant or intermediate is approached from both sides by an attacking species

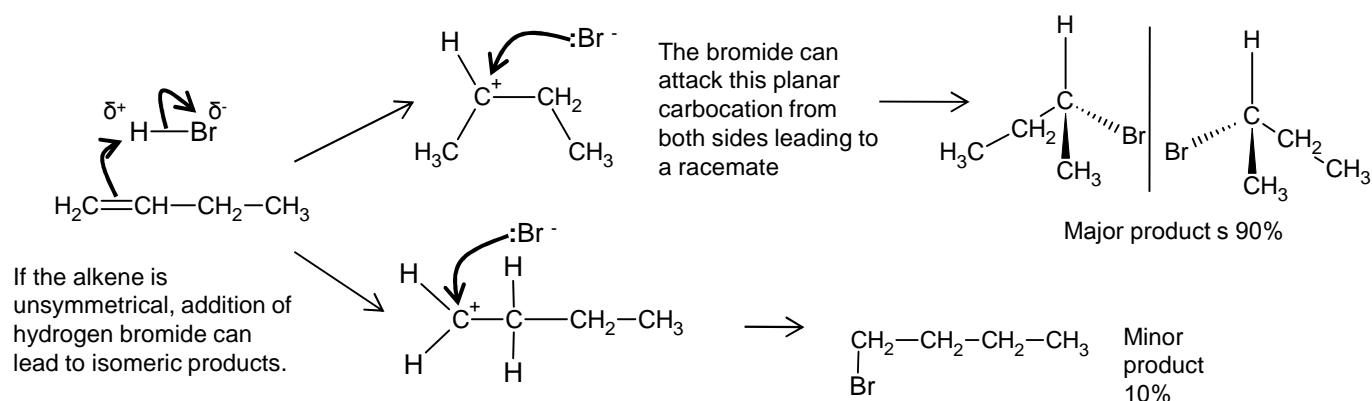


Nucleophilic addition of HCN to aldehydes and ketones (unsymmetrical) when the trigonal planar carbonyl is approached from both sides by the HCN attacking species: results in the formation of a racemate

Mechanism for the reaction (drawn the same for both enantiomers)



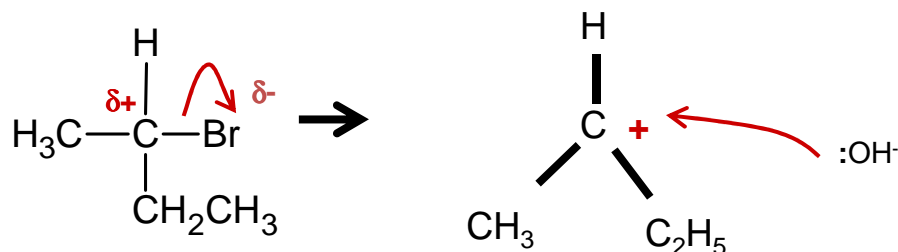
A racemate can also be formed in the reaction of the electrophilic addition of HBr to an unsymmetrical alkene



Nucleophilic substitution reactions and optical activity

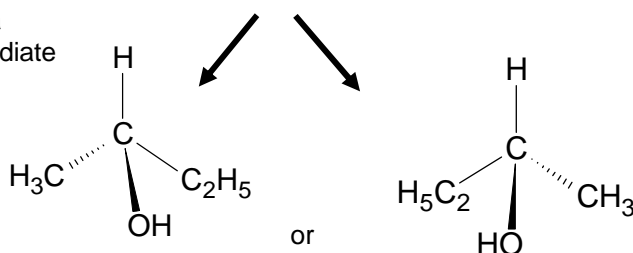
In the topic of reactions of halogenoalkanes we look at the nucleophilic substitution reactions of halogenoalkanes with aqueous hydroxide ions to form alcohols. The reaction can occur via two different mechanisms called SN1 and SN2. Primary halogenoalkanes tend to undergo the SN2 mechanism and tertiary halogenoalkanes undergo the SN1 mechanism. Secondary halogenoalkanes can undergo either mechanism. The two different mechanisms have a different effect on optical activity of chiral reactants. By observing the differing effects it can give us evidence for which mechanism is occurring.

Nucleophilic substitution mechanism, SN1

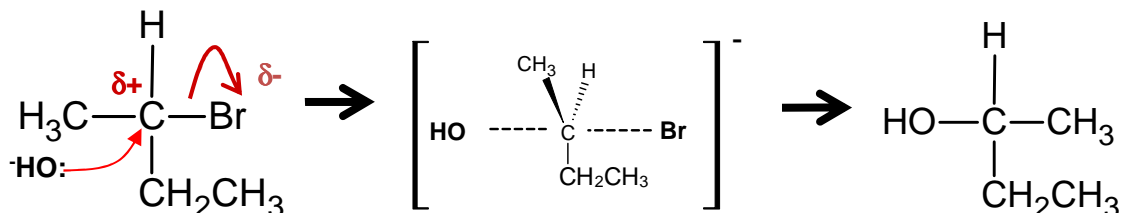


The OH⁻ ion can then attack from either side resulting in different enantiomers and a **racemate forms**

The Br breaks off leaving a planar carbocation intermediate

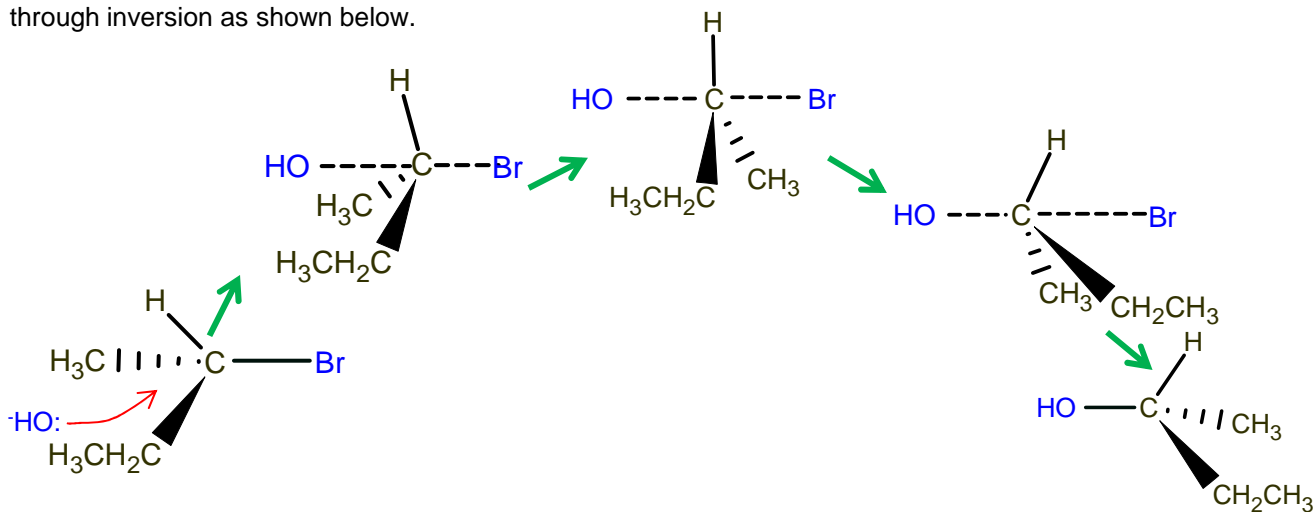


Nucleophilic substitution mechanism, SN2



In the SN₂ mechanism no intermediates are formed and the reaction occurs via a transition state

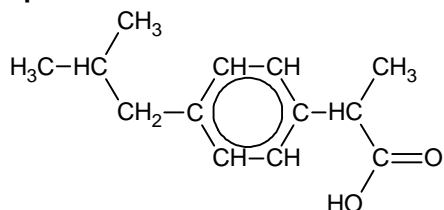
If the reactant was chiral then during the reaction the **opposite enantiomer** would form through inversion as shown below.



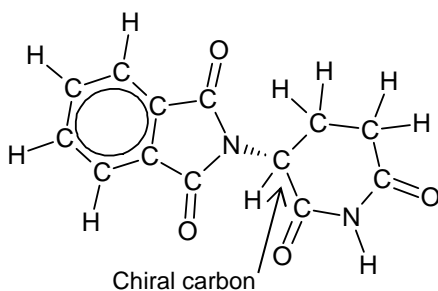
Drug action and optical isomers

Drug action may be determined by the stereochemistry of the molecule.
Different optical isomers may have very different effects

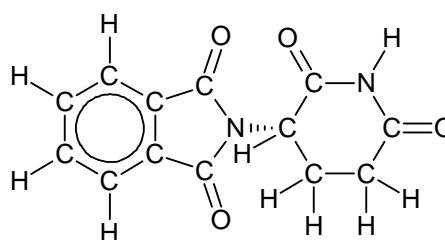
Ibuprofen



Thalidomide



R thalidomide (dangerous drug)



S thalidomide (effective drug)

One enantiomer of thalidomide causes birth defects in unborn children whilst the other had useful sedative properties. It was used as a drug to treat pregnant women with morning sickness. At the time the side effect was not known. Unfortunately it was given in a racemic mixture when first used and many babies were born with birth defects