Edexcel International A Level (IAL) Chemistry

Your notes

Organic Chemistry: Chirality

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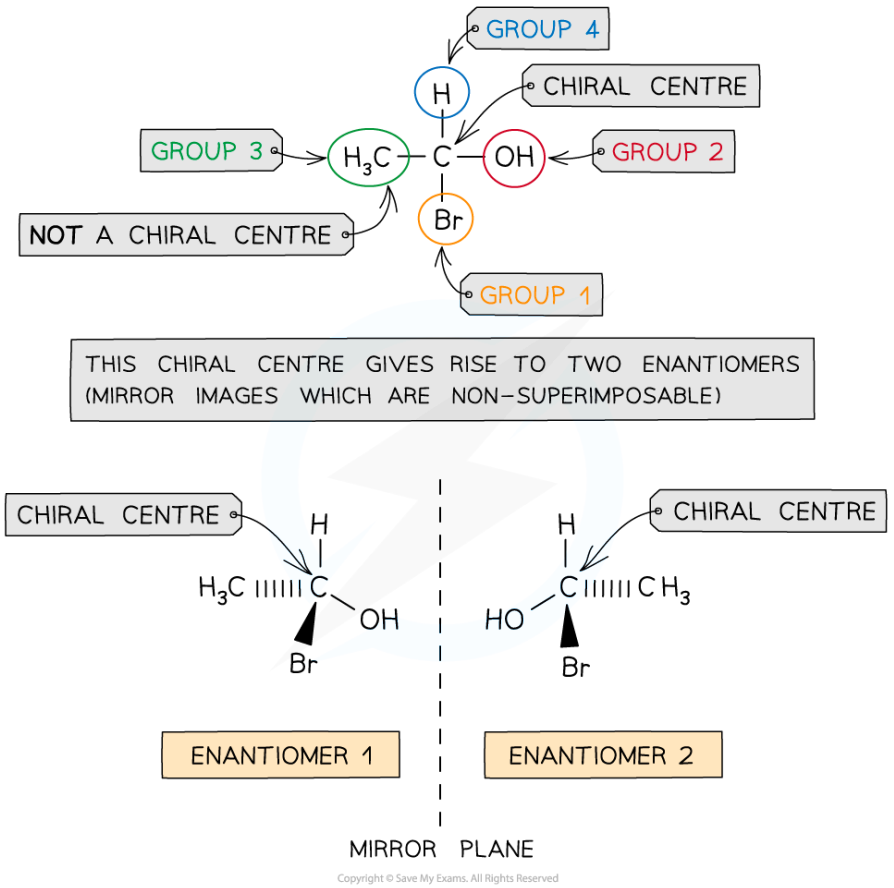
Chirality in Optical Isomers

Optical isomers

- A carbon atom that has four different atoms or groups of atoms attached to it is called a **chiral carbon** or **chiral centre**
  - Chira comes from a Greek word meaning hand, so we talk about these molecules having a handedness
- The carbon atom is described as being **asymmetric**, i.e. there is no plane of symmetry in the molecule
- Compounds with one chiral centre (**chiral molecules**) exist as two optical isomers, also known as **enantiomers**
- Just like the left hand cannot be superimposed on the right hand, enantiomers are **non-superimposable**
  - Enantiomers are **mirror images** of each other



A molecule has a chiral centre when the carbon atom is bonded to four different atoms or group of atoms; this gives rises to enantiomers

- You always obtain two optical isomers from one chiral centre
- Where a molecule has two chiral centres, then there are two pairs of optical isomers
- The isomers will only differ in two characteristics; how they interact with plane polarised light and how they react with other chiral molecules
- If a molecule has three chiral centres there will be eight stereoisomers
- This means the relationship is: number of isomers = 2^n where n= the number of chiral centres

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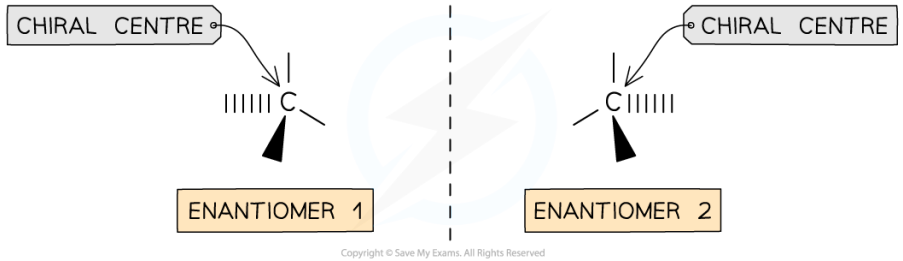
Examiner Tips and Tricks

When drawing optical isomers, always draw mirror images including wedge and dashed bonds



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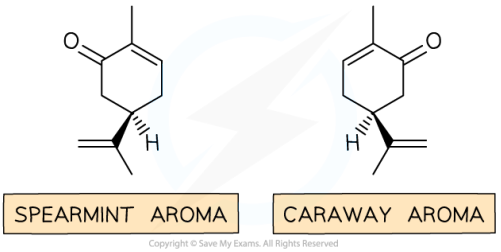
Racemates & Optical Activity

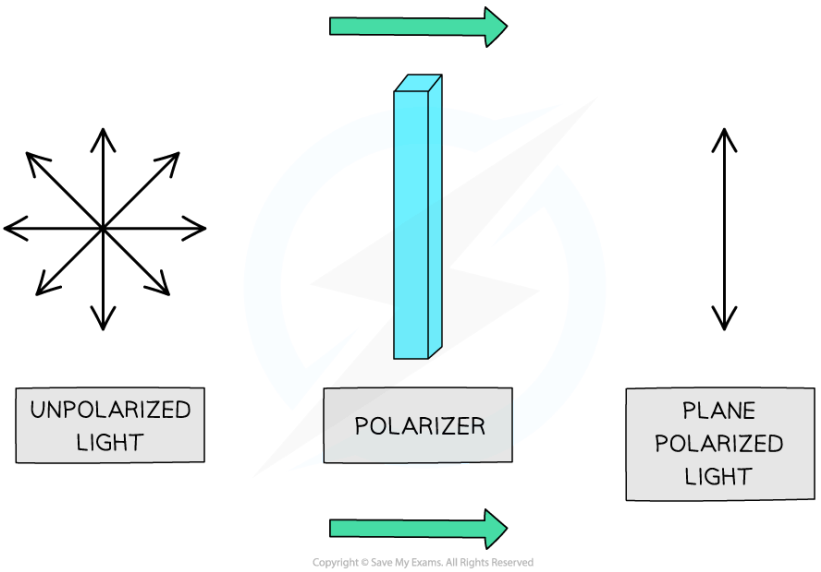
Properties of optical isomers

- The chemical properties of optical isomers are generally identical, with one exception
  - Optical isomers interact with biological sensors in different ways
    - For example, one enantiomer of carvone smells of spearmint, while the other smells of caraway



Carvone optical isomers have distinctive smells

- Optical isomers have identical physical properties, with one exception
  - Isomers differ in their ability to rotate the plane of polarised light

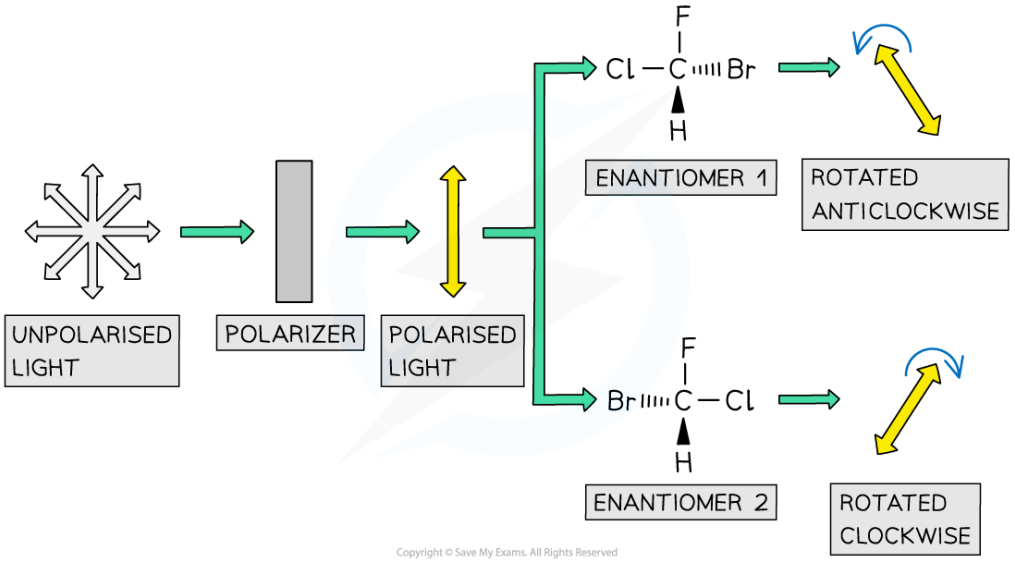


When unpolarised light is passed through a polariser, the light becomes polarised as the waves will vibrate in one plane only

- The major difference between the two enantiomers is:

- One enantiomer rotates plane polarised light in a **clockwise** manner and the other in an **anticlockwise** fashion
- A common way to differentiate the isomers is to use (+) and (-), but there are other systems using d and l, D and L, or R and S

- The rotation of plane polarised light can be used to determine the identity of an optical isomer of a single substance
  - For example, pass plane polarised light through a sample containing one of the two optical isomers of a single substance
  - Depending on which isomer the sample contains, the plane of polarised light will be rotated either clockwise or anti-clockwise by a fixed number of degrees



Each enantiomer rotates the plane of polarised light in a different direction

- A **racemic mixture** (or **racemate**) is a mixture containing **equal amounts** of each enantiomer
  - One enantiomer rotates light clockwise, the other rotates light anticlockwise
- A racemic mixture is **optically inactive** as the enantiomers will cancel out each others effect
  - This means that the plane of polarised light will **not change**

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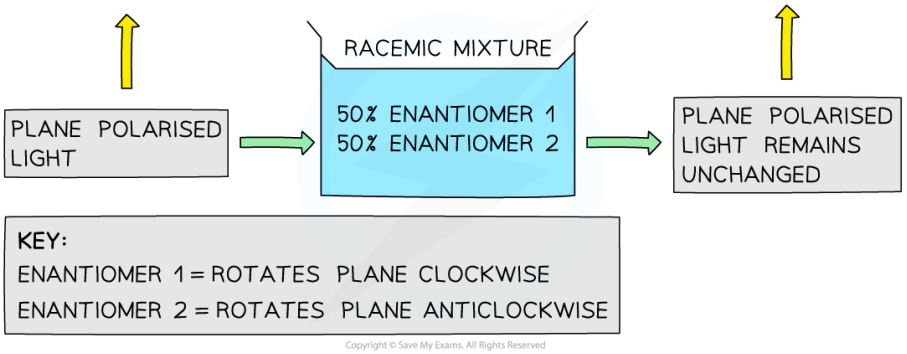
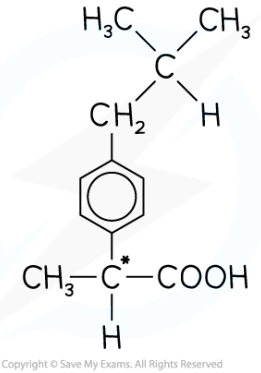


Racemic mixtures are optically inactive

Racemic mixtures and drugs

- In the pharmaceutical industry, it is much easier to produce synthetic drugs that are racemic mixtures than producing one enantiomer of the drug
- Around 56% of all drugs in use are chiral and of those 88% are sold as racemic mixtures
- Separating the enantiomers gives a compound that is described as **enantiopure**, it contains only one enantiomer
- This separation process is very expensive and time consuming, so for many drugs it is not worthwhile, even though only half the of the drug is pharmacologically active
- For example, the pain reliever ibuprofen is sold as a racemic mixture



The structure of ibuprofen showing the chiral carbon that is responsible for the racemic mixture produced in the synthesis of the drug

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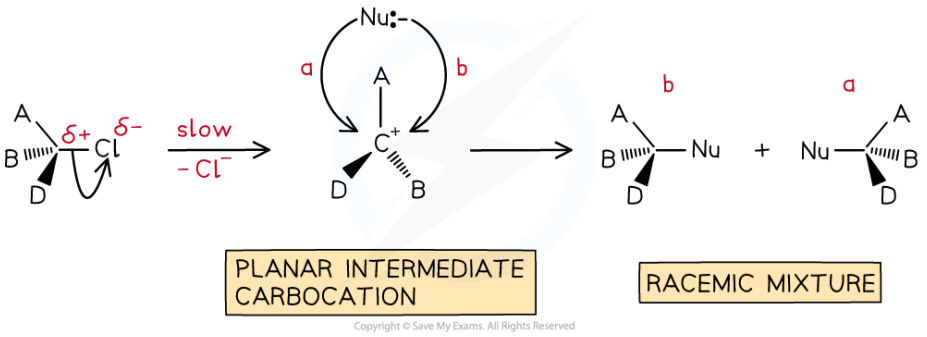
Mechanisms & Optical Activity

- Optical activity can be used to suggest the mechanism of a chemical reaction
- This is particularly the case for **nucleophilic substitution**
  - Nucleophilic substitution can occur via an S_N1 or S_N2 mechanism

S_N1 mechanism

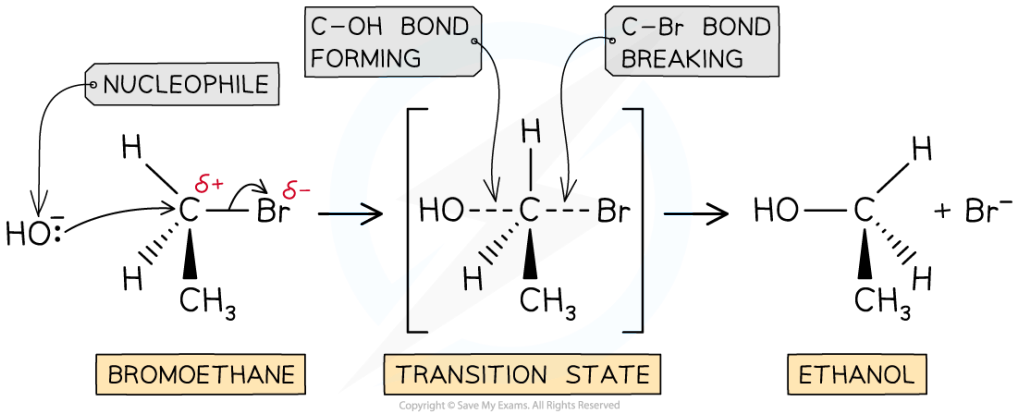
- The S_N1 mechanism is a **two-step** reaction
  - In the first step, the C-X bond breaks heterolytically and the halogen leaves the halogenoalkane as an X^- ion
  - This leaves a **trigonal planar**, tertiary carbocation
  - In the second step, the planar, tertiary carbocation is attacked by the nucleophile
  - **The nucleophile is able to attack from either side of the planar carbocation, which results in the formation of a racemic mixture**
- Therefore, a reaction with an S_N1 mechanism will produce a racemic mixture



S_N1 Optical Isomers Mechanism

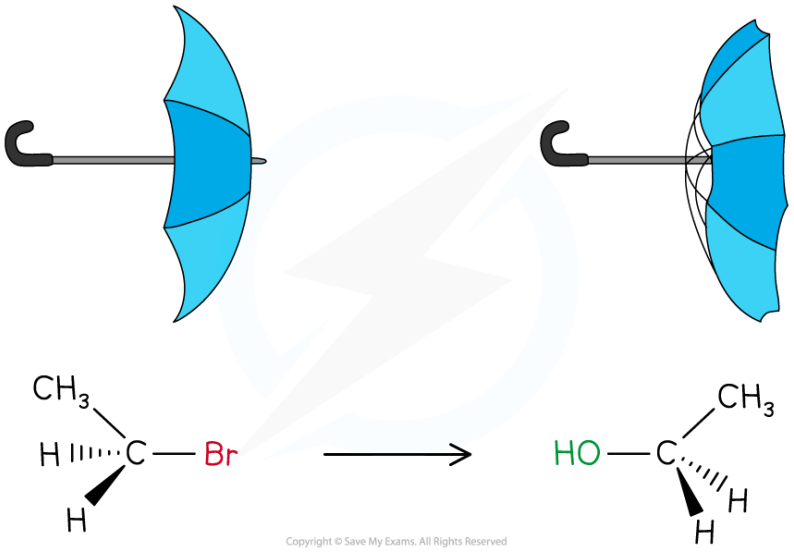
S_N2 mechanism

- The S_N2 mechanism is a **one-step** reaction
  - The nucleophile donates a pair of electrons to the δ+ carbon atom of the halogenoalkane to form a new bond
  - At the same time, the C-X bond is breaking and the halogen (X) takes both electrons in the bond
  - The halogen leaves the halogenoalkane as an X^- ion
- For example, the nucleophilic substitution of bromoethane by hydroxide ions to form ethanol



The S_N2 mechanism of bromoethane with hydroxide causing an inversion of configuration

- The bromine atom of the bromoethane molecule causes **steric hindrance**
- This means that the hydroxide ion nucleophile can only attack from the opposite side of the C-Br bond
  - Attack from the same side as the bromine atom is sometimes called frontal attack
  - While attack from the opposite side is sometimes called backside or rear-side attack
- As the C-OH bond forms, the C-Br bond breaks causing the bromine atom to leave as a bromide ion
  - As a result of this, the molecule has undergone an inversion of configuration
  - The common comparison for this is an umbrella turning inside out in the wind



Inversion of configuration – umbrella analogy

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- Therefore, if a reaction with an S_N2 mechanism starts with an enantiopure reactant then an enantiopure products will be formed

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