CIE A Level Chemistry

Your notes

13.4 Isomerism: Structural Isomerism & Stereoisomerism

Contents

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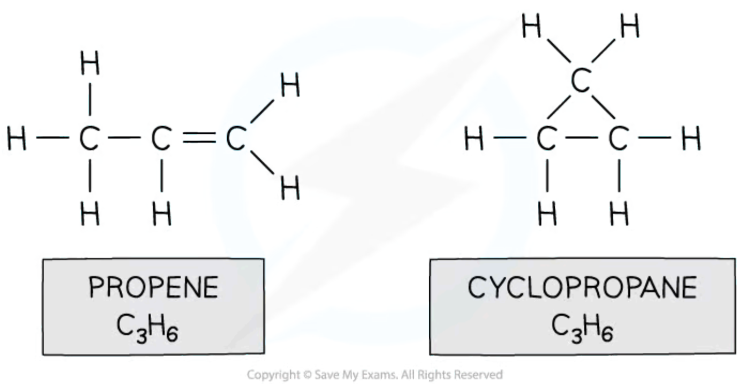
Structural Isomerism

Structural Isomerism: Chain, Position & Functional Group

- **Structural isomers** are compounds that have the same **molecular** formula but different **structural** formulae
  - E.g. propene and cyclopropane

C_3H_6 structural isomers



Both propene and cyclopropane are made up of 3 carbon and 6 hydrogen atoms but the structure of the two molecules differs

- There are three different types of structural isomerism:
  - **Chain** isomerism
  - **Positional** isomerism
  - **Functional** group isomerism

Chain isomerism

- **Chain isomerism** is when compounds have the same molecular formula, but their longest hydrocarbon chain is not the same
- This is caused by branching
  - E.g. pentane and 2,2-dimethylpropane

C_5H_{12} branch / chain isomers

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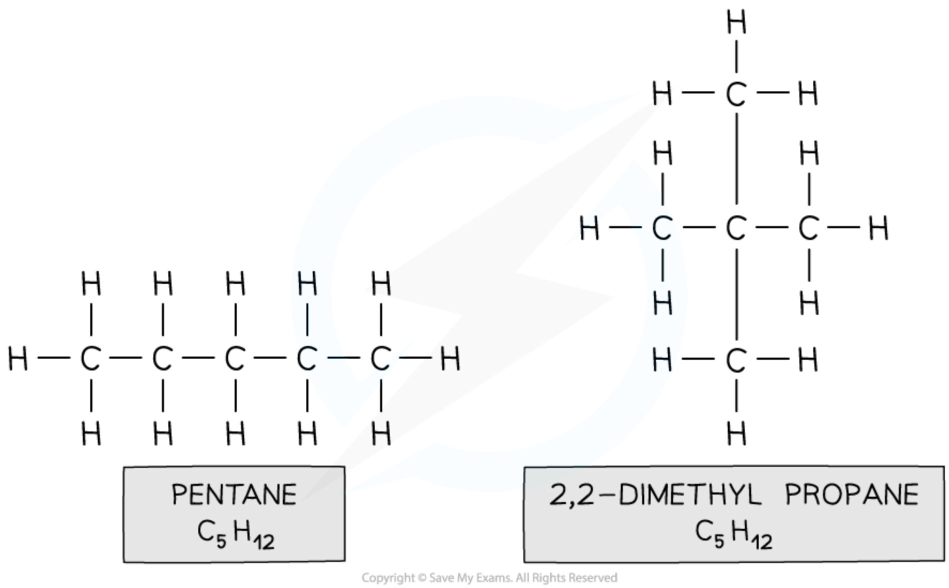
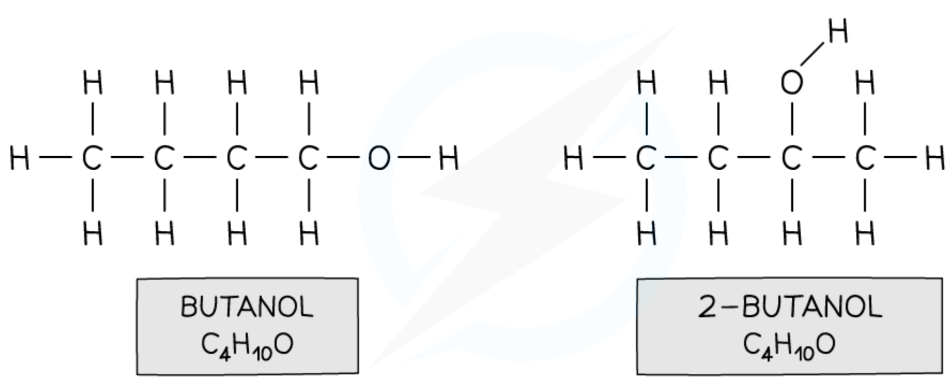


Both compounds are made up of the same atoms however the longest carbon chain in pentane is 5 and in 2,2-dimethylpropane 3 (with two methyl branches)

Positional isomerism

- **Positional isomers** arise from differences in the position of a functional group in each isomer
  - The functional group can be located on different carbons
  - E.g. butan-1-ol and butan-2-ol / 2-butanol

$C_4H_{10}O$ positional isomers



Both compounds have an alcohol group and are made up of 4 carbon, 10 hydrogen and one oxygen atom however in butan-1-ol the functional group is located on the first carbon and in butan-2-ol on the second carbon

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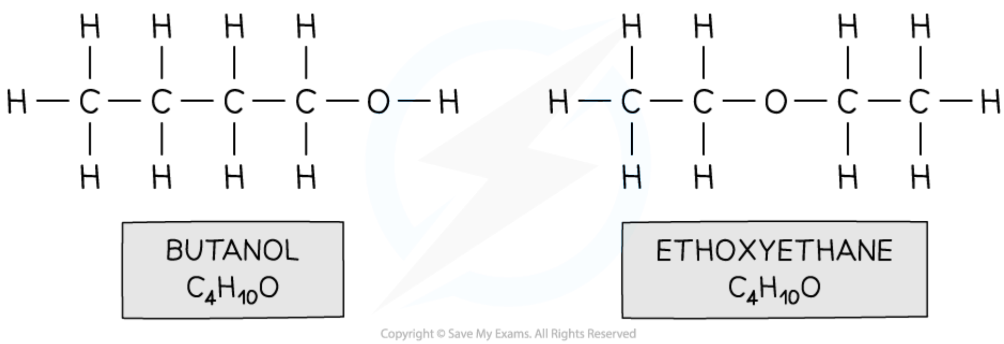
Functional group isomerism

- When different functional groups result in the same molecular formula, **functional group isomers** arise
- The isomers have very different chemical properties as they have different functional groups
  - E.g. butan-1-ol and ethoxyethane

$C_4H_{10}O$ functional group isomers



Both compounds have the same molecular formula however butanol contains an alcohol functional group and ethoxyethane an ether functional group

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Stereoisomerism

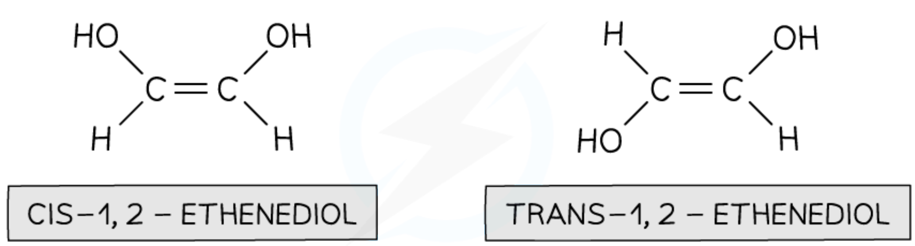
Stereoisomerism: Geometrical & Optical

- **Stereoisomers** are compounds that have the same atoms connected to each other, however the atoms are differently arranged in space
- There are two types of **stereoisomerism**:
  - Geometrical (cis/trans) isomerism
  - Optical isomerism

Geometrical (cis/trans) isomerism

- **Geometrical isomerism** is seen in unsaturated (double bond containing) or ring compounds that have the same molecular formula and order of atoms (the atoms are connected similarly to each other) but different shapes
- **Cis/trans** nomenclature is used to distinguish between the isomers
  - Cis isomers have functional groups on the same side of the double bond/carbon ring
  - Trans isomers have functional groups on opposite sides of the double bond/carbon ring

Geometrical isomerism in unsaturated compounds



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cis isomers have both functional groups above or both below the C=C bond. Trans isomers have one functional group above and one functional group below the C=C bond

Geometrical isomerism in cyclic compounds

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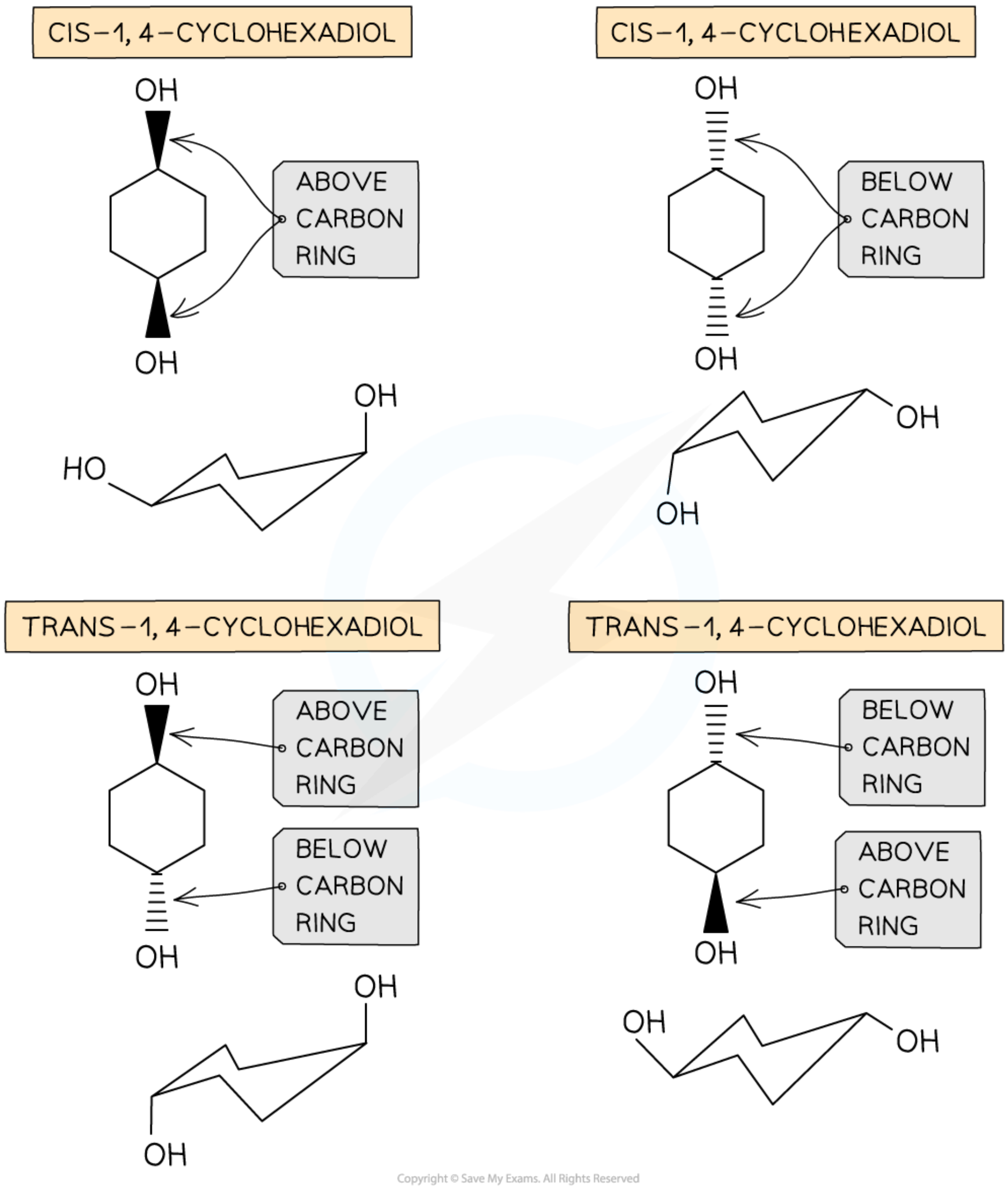

The same principle of cis and trans applies to cyclic compounds, where cis means both functional groups above or below the ring structure and trans means one functional group above and the other below the ring structure

- This causes the compounds to have different **chemical** and **physical** properties

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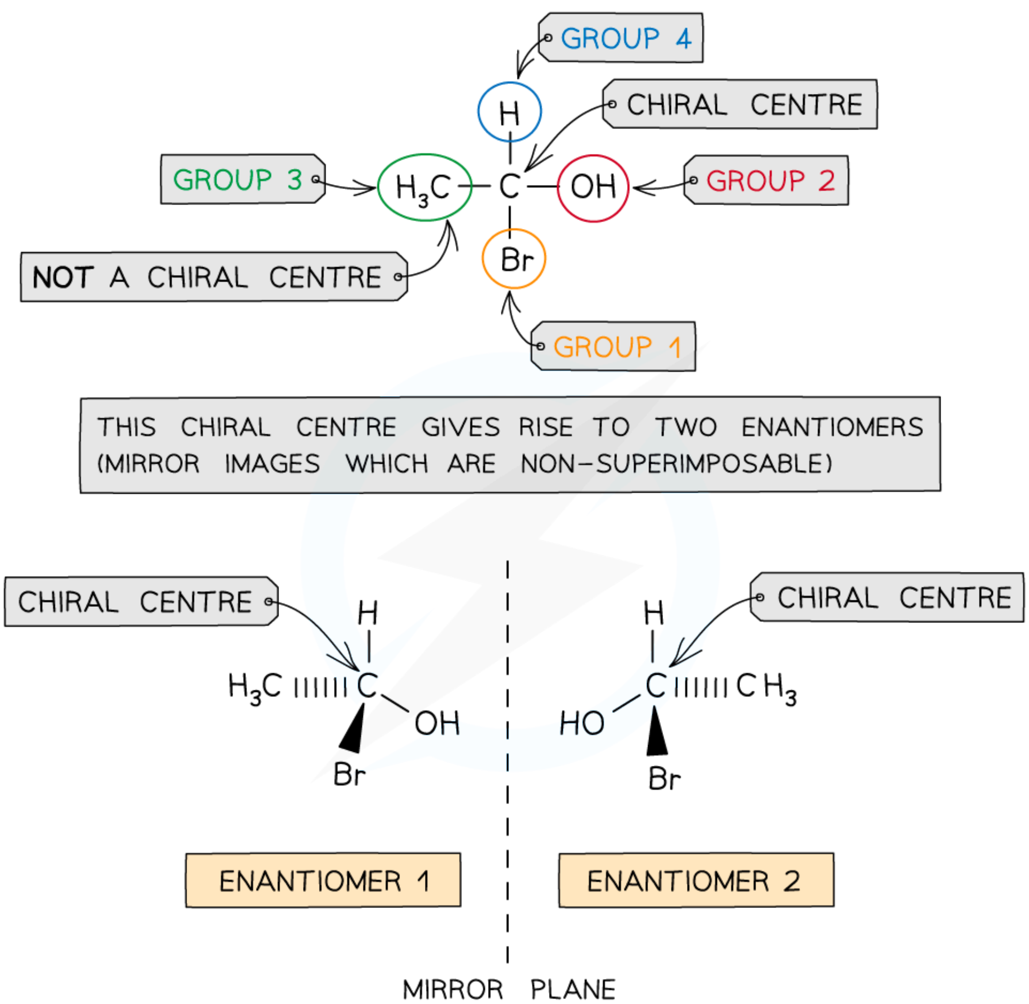
- For example, they may have different reaction rates for the same reaction (chemical property) or different melting/boiling points (physical property)

Optical isomerism

- **Optical isomers** arise when a carbon atom in a molecule is bonded to four different atoms or groups of atoms
- The carbon atom is 'asymmetric' as there is no plane of symmetric in the molecule and is also called the **chiral centre** of the molecule
- Just like the left hand cannot be **superimposed** on the right hand, enantiomers too are **non-superimposable**
- Enantiomers are **mirror images** of each other.
- The two different optical isomers are also called **enantiomers**

Optical isomers



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Both molecules are made up of the same atoms which are bonded to each other identically, however the chiral centre (carbon with four different groups) gives rise to optical isomerism

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- Optical isomers differ in their ability to rotate the **plane of polarised light**
  - One enantiomer will rotate it **clockwise** and the other **anticlockwise**

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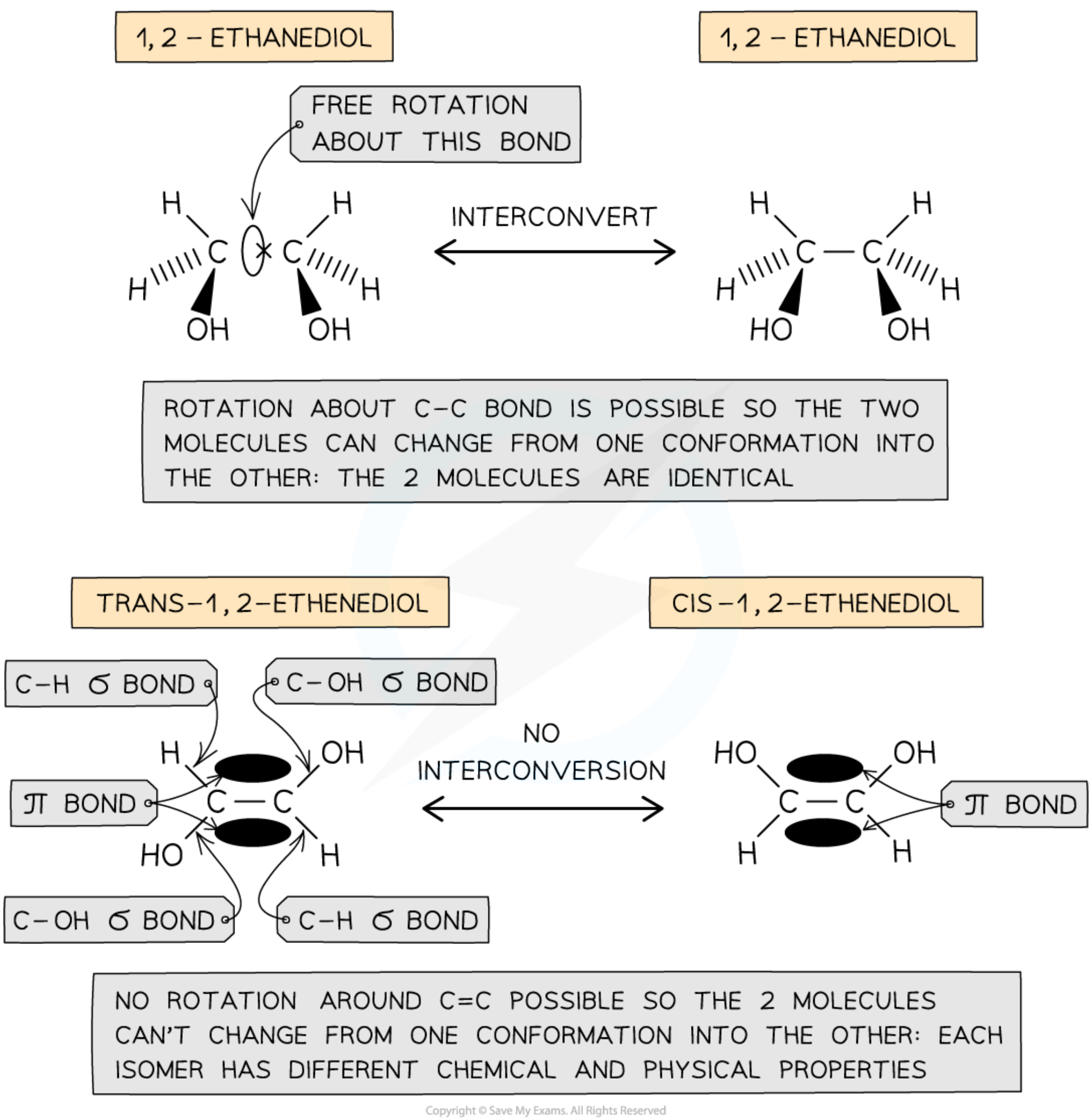
Geometrical Isomerism in Alkenes

Unsaturated compounds

- In unsaturated compounds, the groups attached to the C=C carbons remain fixed in their position
- This is because free rotation of the bonds about the C=C bond is not possible due to the presence of a π bond

Explaining cis and trans geometric isomerism



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The presence of a π bond in unsaturated compounds restricts rotation about the C=C bond forcing the groups to remain fixed in their position and giving rise to the formation of geometrical isomers

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Examiner Tip

Geometrical isomerism is also possible in **cyclic compounds** because there is limited rotation about C-C single bonds that make up the rings

Therefore, the substitutions in cyclic compounds are fixed in their position (to stay either above or below the ring of carbon atoms)

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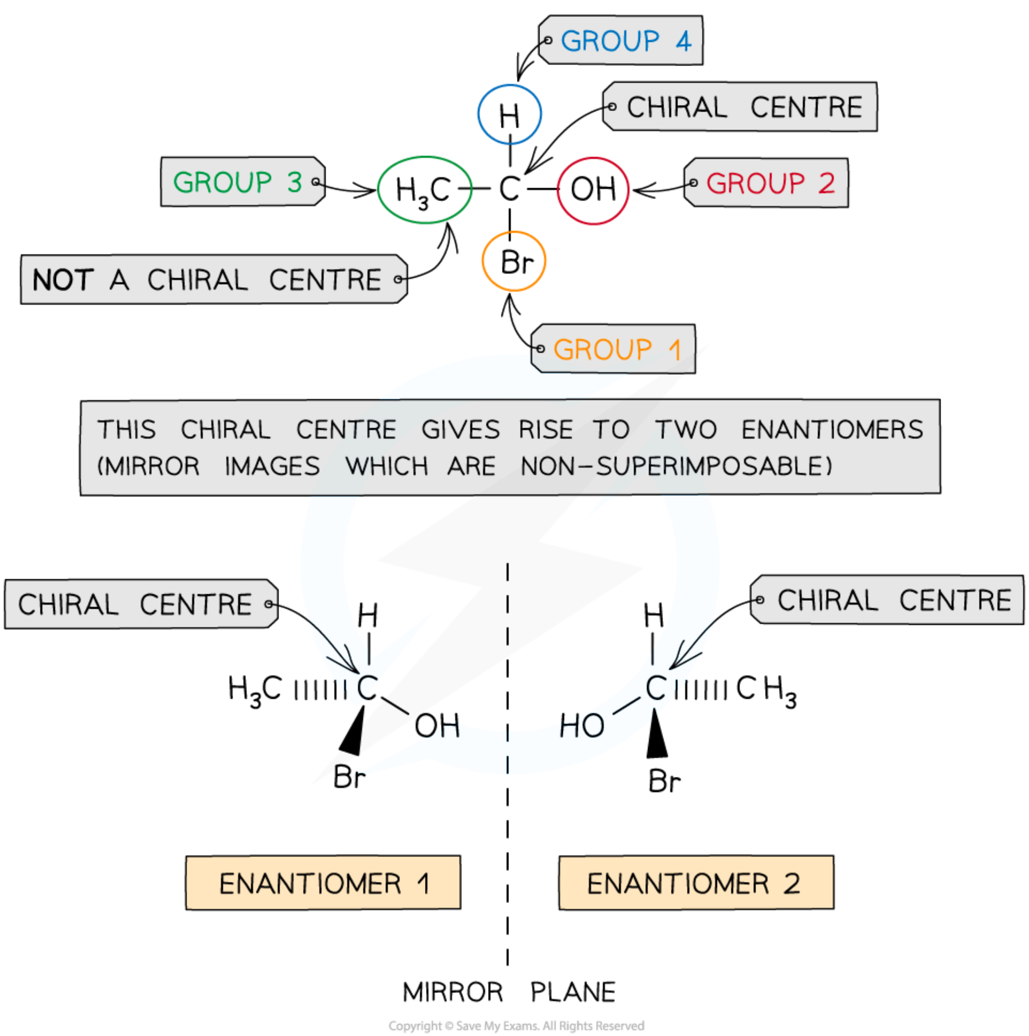
Chirality

Chirality & Enantiomers

Chiral centres in non-cyclic molecules

- A **chiral centre** in a molecule is a carbon atom that has four different atoms or groups of atoms attached
- This gives rise to two optical isomers which are also called **enantiomers**
- The enantiomers are **mirror images** of each other and cannot be superimposed

Chiral centres in non-cyclic molecules



The presence of the chiral centre in the molecule allows two enantiomers to exist which are stereoisomers as the molecules have the same atoms bonded to each other, but they are differently

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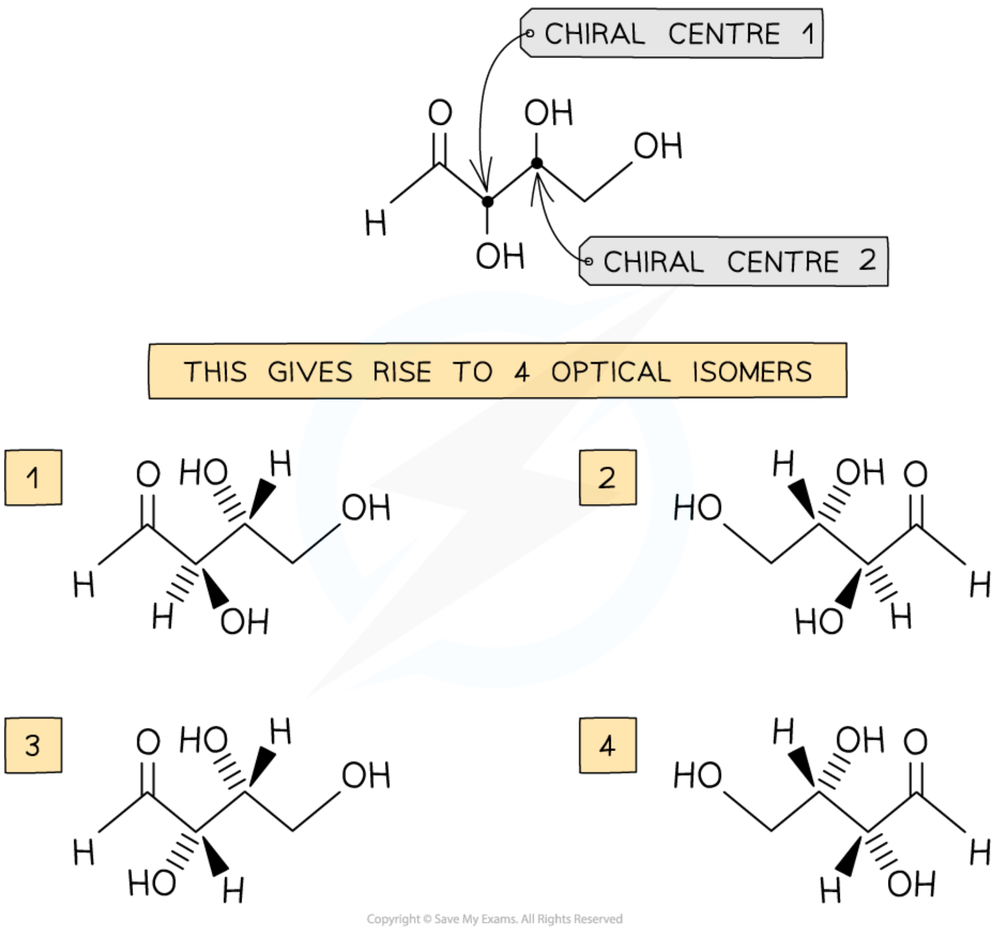
arranged in space

- When the molecule contains more than one chiral centre (asymmetric carbon) more than two optical isomers will be formed
  - If there are two chiral centres, each chiral centre will rotate the plane of polarised light clockwise and anticlockwise
  - There are **four** possible optical isomers

Molecules with multiple chiral centres



Each chiral centre gives rise to two optical isomers; therefore, the molecule has a total of four optical isomers

Chiral centres in cyclic molecules

- To determine the chiral centre in a cyclic molecule, the carbon bonded to four different atoms or groups of atoms should be found
  - E.g. 2-aminocyclohexanol has two chiral centres so it can form four optical isomers

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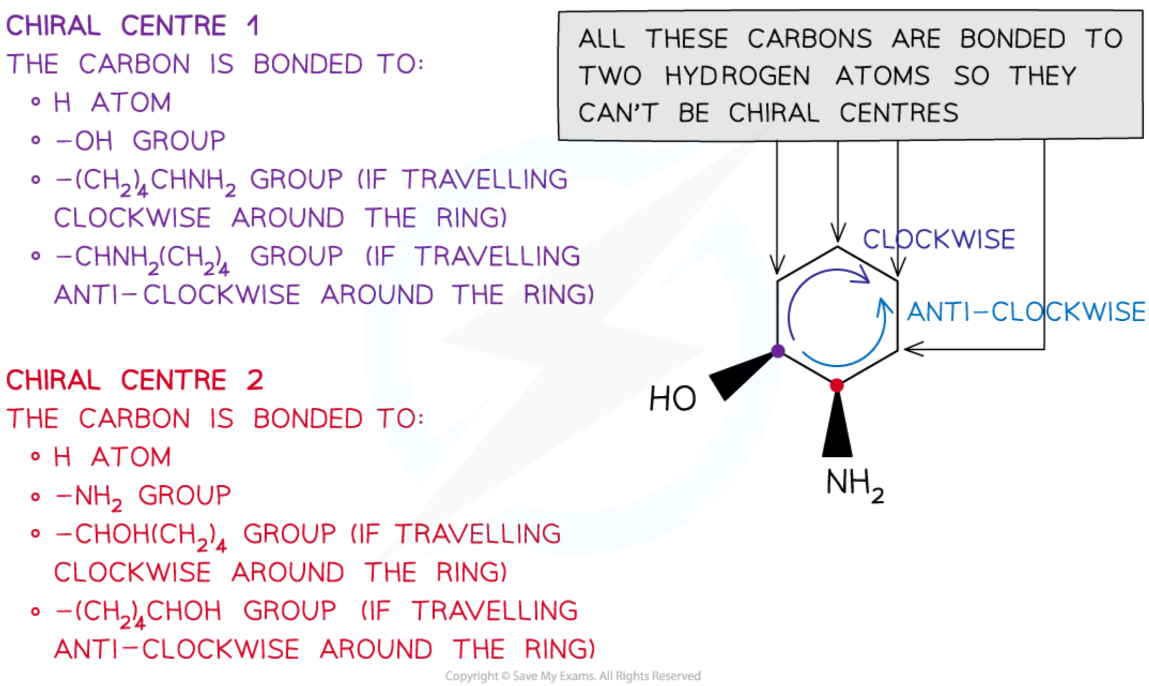
Chiral centres in cyclic molecules



To decide where the chiral centres are in a cyclic molecule, the carbon atoms bonded to four different atoms or atom groups should be found

Examiner Tip

Use a **molecular modelling kit** and make the models of enantiomers to help you understand that the two molecules are non-superimposable and therefore non-identical

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Identifying Chirality & Geometrical Isomerism

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Identify chirality

- Identifying **chiral centres** in cyclic and non-cyclic compounds is very straightforward as it is the carbon with four different atoms or atom groups in a molecule
- This gives rise to **two** optical isomers
- When more than two chiral centres are present, more than two optical isomers exist
  - The maximum number of stereoisomers that a molecule can have is 2^n, where n is the number of chiral centres
- So, a molecule with **three** chiral centres will have 2^3 = **eight** optical isomers
- A molecule containing chiral centres is called a **chiral molecule**

Identifying geometrical isomers

- Molecules with restricted rotation about the C-C bond can have geometrical isomers
- This includes unsaturated and cyclic compounds
  - E.g. alkenes and cyclopentane
- When the groups are positioned on the same side of the C-C double bond, the compound is a **cis** isomer
- When the groups are positioned on opposite sides of the C-C double bond the compound is a **trans** isomer

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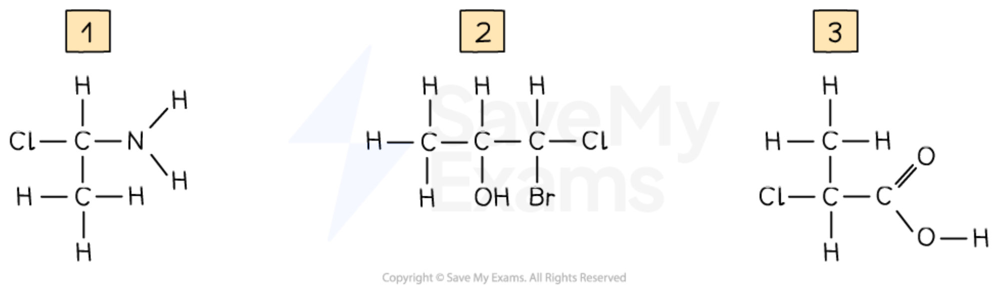
Worked example

Drawing optical isomers

Draw the optical isomers of the following compounds:



Answers:

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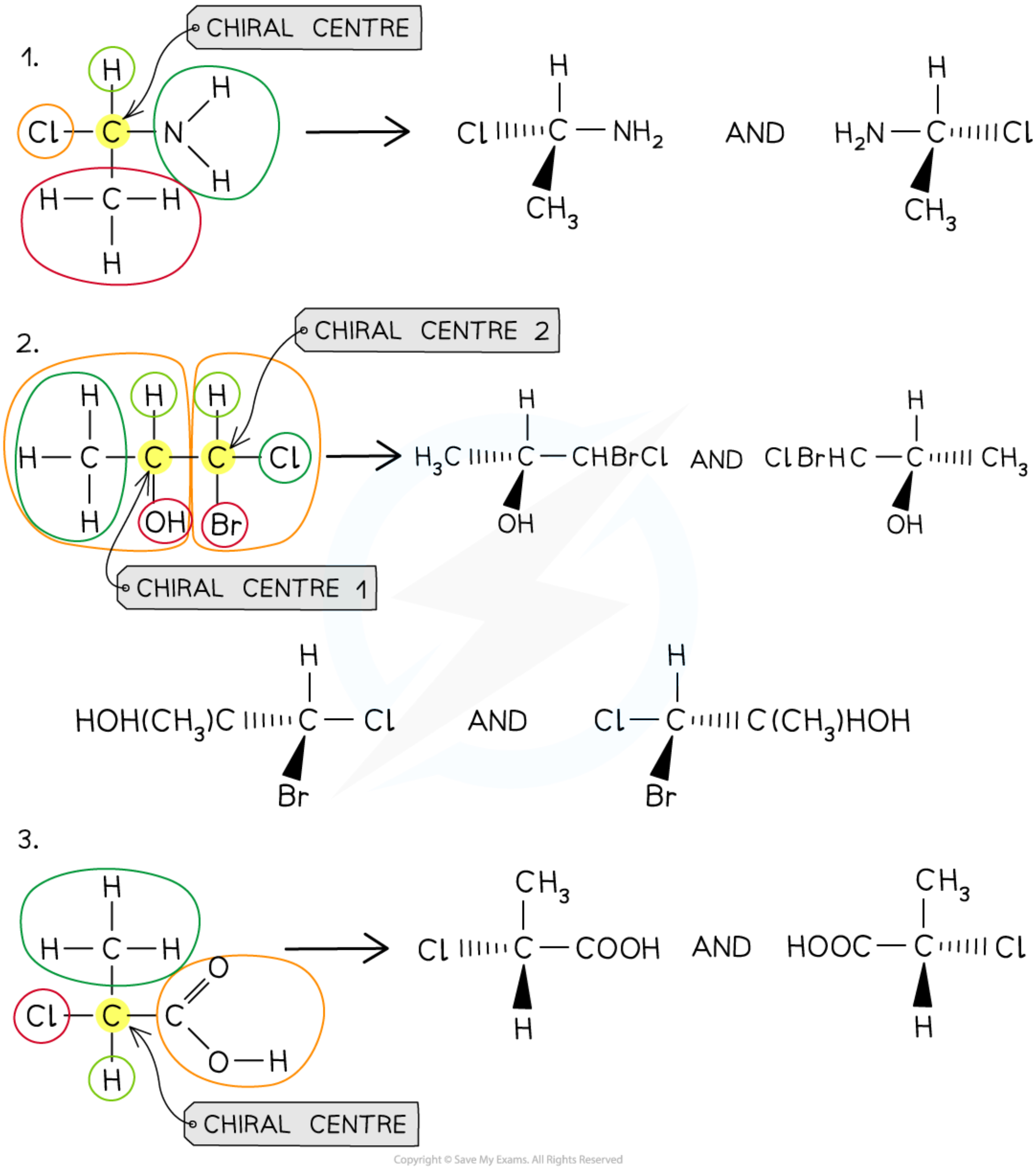

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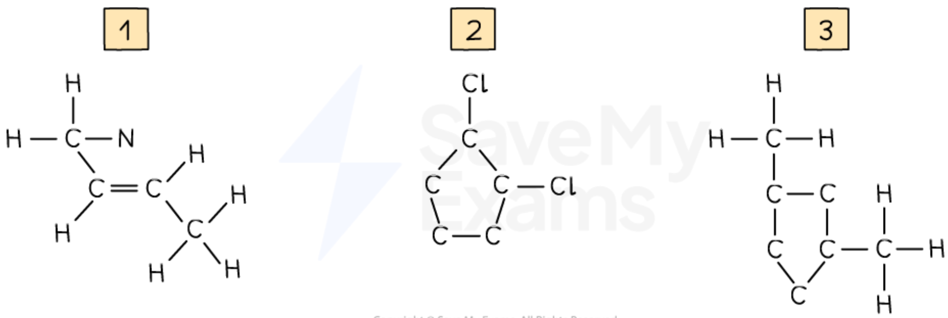
Your notes

Worked example

Drawing geometrical isomers

Draw the geometrical isomers of the following compounds:



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Answers:

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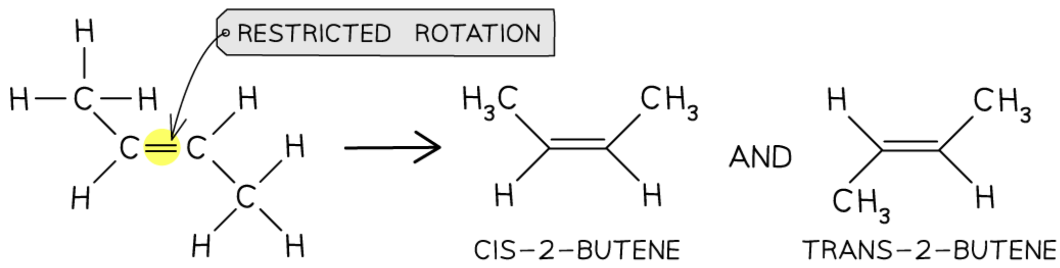
1.



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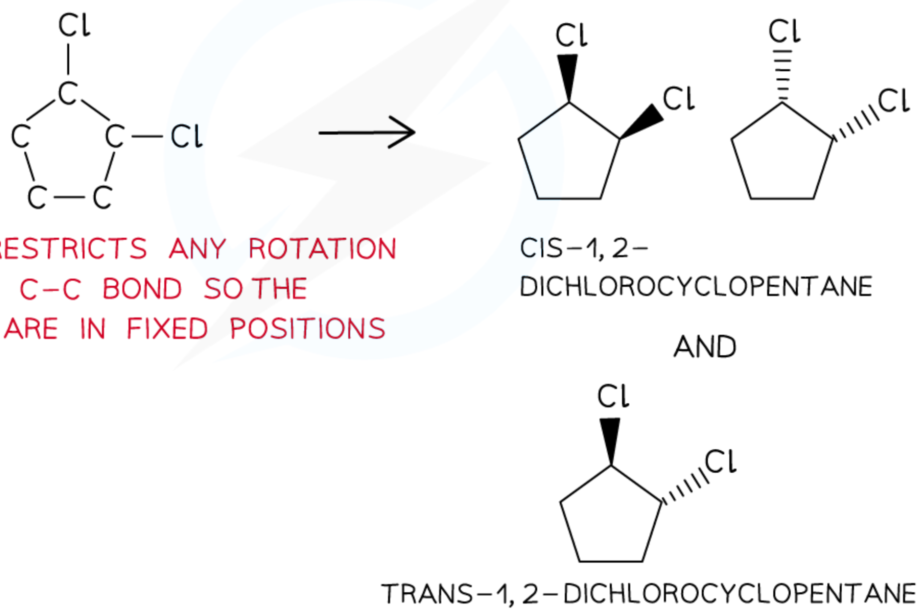

THE RING RESTRICTS ANY ROTATION ABOUT THE C–C BOND SO THE CHLORINES ARE IN FIXED POSITIONS

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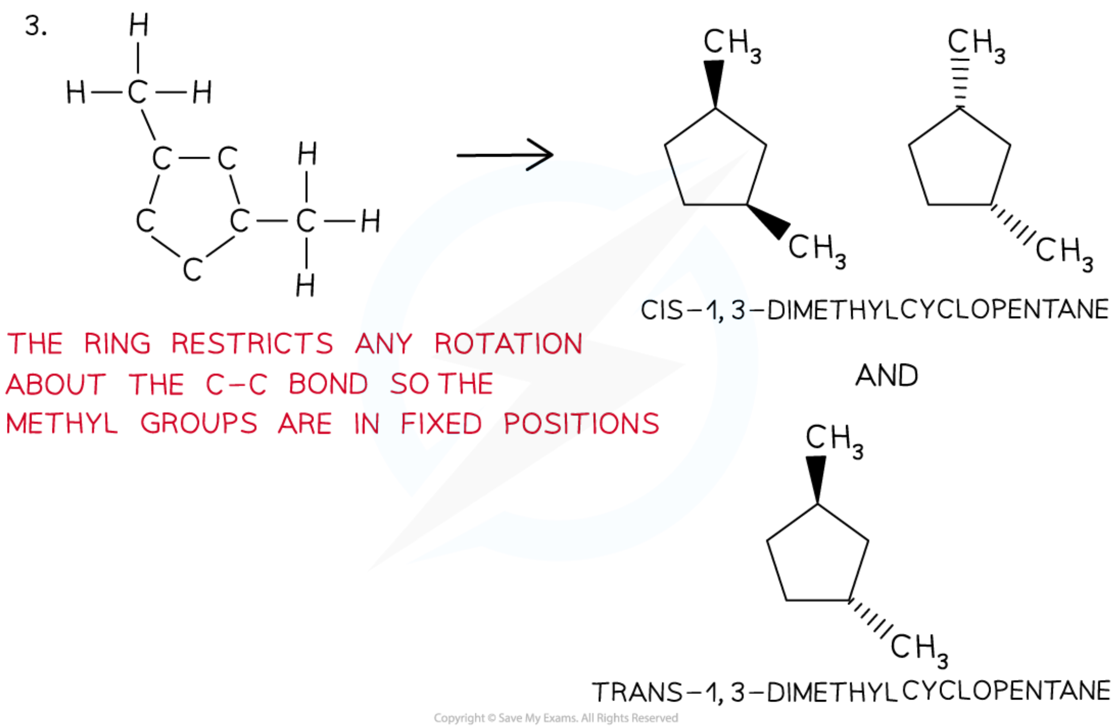

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Isomers of Organic Compounds

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Deducing Isomers of a Compound

- You should be able to deduce all possible isomers for organic compounds knowing their molecular formula

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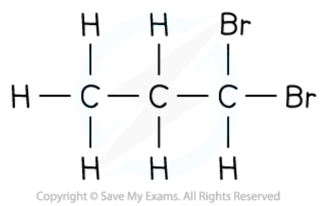
Worked example

How many isomers are there of dibromopropane, $C_3H_6Br_2$?

Answer

Step 1: Draw the structural formula of the compound

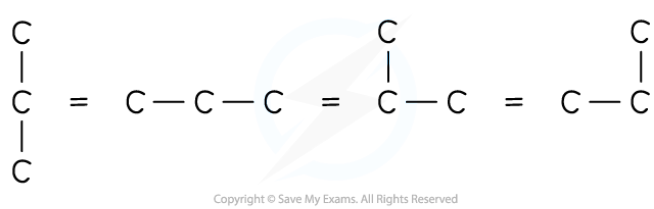


Step 2: Determine whether it is a stereo or structural isomer

There is no restricted bond rotation around the C-C bond, so it is structural isomerism

Step 3: Determine whether it is a functional group, chain or positional isomerism

- Functional group? No, as Br is the only functional group possible
- Chain? No, as the longest chain can only be 3
- Positional? Yes, as the two bromine atoms can be bonded to different carbon atoms



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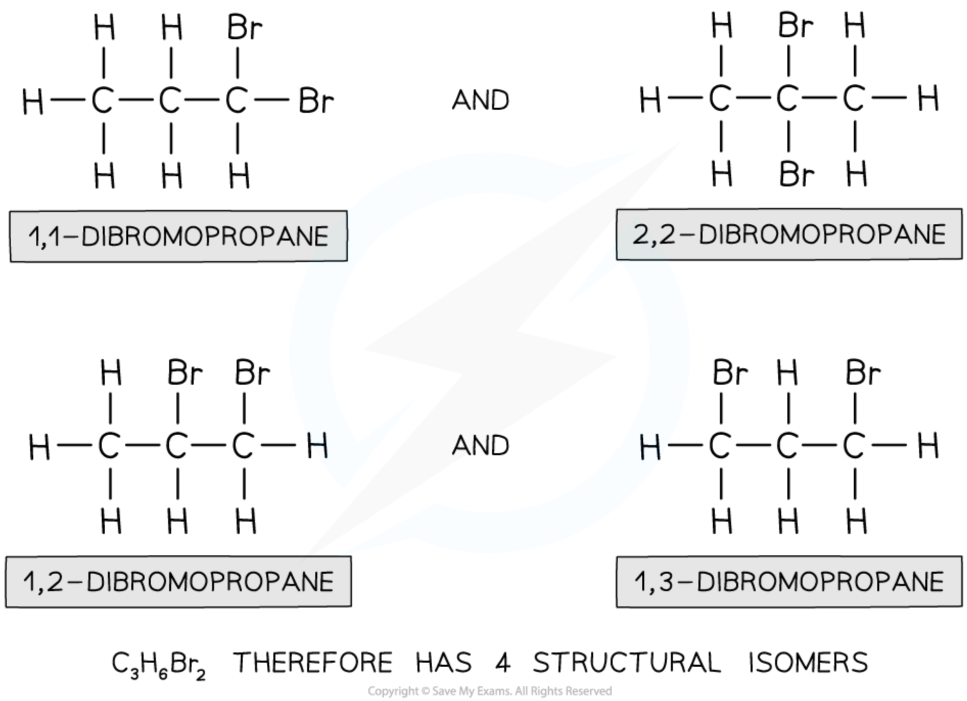

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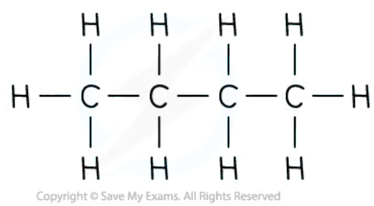
Worked example

How many isomers are there of the compound with molecular formula C_4H_{10}?

Answer:

- **Step 1:** Draw the structural formula of the compound



- **Step 2:** Determine whether it is a stereo or structural isomer.

  There is no restricted bond rotation around the C-C bond and there is no chiral centre so it is structural isomerism

- **Step 3:** Determine whether it is a functional group, chain or positional isomerism
  - Functional group? No, as there are no functional groups
  - Positional? No, as there are no functional groups which can be positioned on different carbon atoms
  - Chain? Yes!

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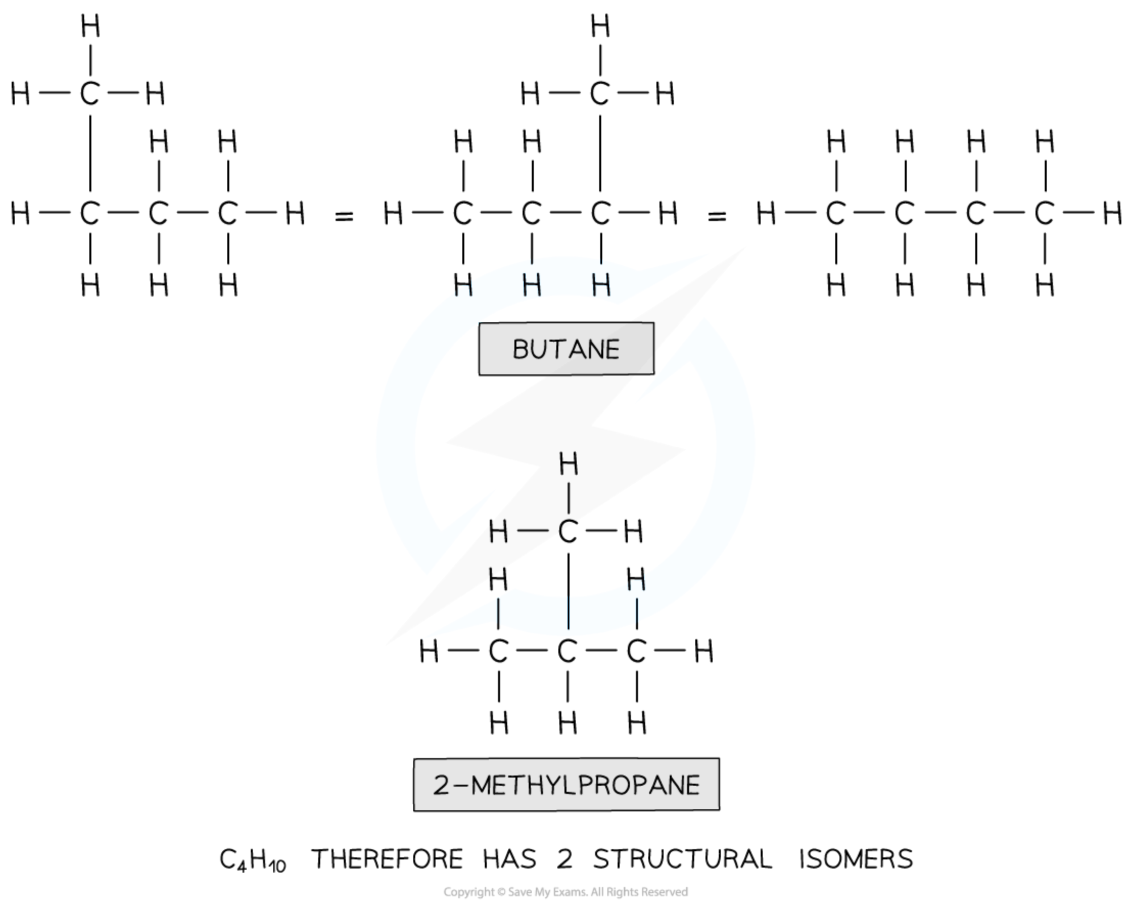

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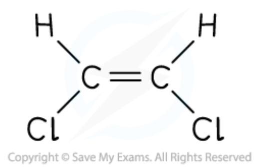
Worked example

How many **stereoisomers** are there of the compound with molecular formula $C_2H_2Cl_2$?

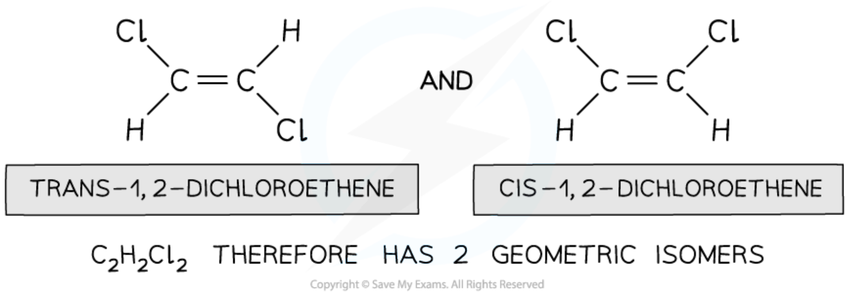
Answer:

- **Step 1:** Draw the possible structural formula of the compound



- **Step 2:** Determine whether it is a stereo or structural isomer
  - The compound has to be unsaturated for it to have molecular formula $C_2H_2Cl_2$
    - Due to the double bond there is restricted rotation about the C-C bond; This compound will therefore display geometrical isomerism
  - **1,1-dichloroethene** is a structural isomer of 1,2 dichloroethene and does not exhibit stereoisomerism

- **Step 3:** Determine whether it is optical or geometrical isomerism
  - Optical? No, as there are no chiral centres
  - Geometric? Yes!



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