$S_N2$ - nucleophilic bimolecular substitution reaction. It is a one-step reaction that involves the formation of an unstable transition state. Primary halogenoalkanes undergo $S_N2$ reactions.
The nucleophile attacks on the opposite side of the leaving group (backside attack).
An unstable transition state is formed in which the carbon is weakly bonded to both the halogen and the nucleophile.
The carbon to halogen bond breaks heterolytically. The backside attack by the nucleophile causes inversion of the atoms around the carbon atom ($S_N2$ reaction is stereospecific).
The reaction conditions are warm with aqueous NaOH

\[ \text{CH}_3\text{CH}_2\text{Cl} + \text{OH}^- \rightarrow \text{CH}_3\text{CH}_2\text{OH} + \text{Cl}^- \]
The $S_{N2}$ reaction is bimolecular; the rate-determining step (slow step) depends on both the concentration of the halogenoalkane and the nucleophile.

\[
\text{rate} = k \ [\text{halogenoalkane}] \ [\text{nucleophile}]
\]

\[
\text{rate} = k \ [\text{CH}_3\text{CH}_2\text{Cl}] \ [\text{OH}^-]
\]
The $S_{N}2$ mechanism is favoured by polar, aprotic solvents.

Aprotic solvents are not able to form hydrogen bonds as they lack O-H or N-H bonds. Suitable solvents include propanone ($\text{CH}_3\text{)_2CO}$ and ethanenitrile ($\text{CH}_3\text{CN}$).
$S_N1$ mechanism
$S_n 1$ - nucleophilic unimolecular substitution reaction. It is a two-step reaction that involves the formation of a carbocation intermediate. Tertiary halogenoalkanes undergo $S_n 1$ reactions.
The presence of the 3 alkyl groups around the carbon–halogen bond make it difficult for an incoming group to attack this carbon (steric hindrance). The C-Br bond breaks heterolytically forming a carbocation intermediate.
In the second step, the nucleophile attacks the carbocation, forming a tertiary alcohol.

\[
C(CH_3)_3Br \xrightarrow{\text{slow}} C(CH_3)_3^+ + Br^-
\]

\[
C(CH_3)_3^+ + OH^- \xrightarrow{\text{fast}} C(CH_3)_3OH
\]
The reaction is unimolecular; the rate-determining step (slow step) depends on the concentration of the halogenoalkane only.

\[ \text{rate} = k \ [\text{halogenoalkane}] \]

\[ \text{rate} = k \ [\text{C(CH}_3)_3\text{Br}] \]
The $S_N1$ mechanism is favoured by polar, protic solvents. Protic solvents are able to form hydrogen bonds as they have O-H or N-H bonds. Suitable solvents include water, alcohols and carboxylic acids.
Stereochemistry of $S_N$ reactions
The $S_N1$ mechanism involves the formation of a carbocation intermediate.

The carbocation formed is $sp^2$ hybridised with a trigonal planar geometry.
The nucleophile can attack on either side of the carbocation intermediate.
The product can have the same stereochemical configuration as the reactant (retention) or opposite configuration (inversion).

This produces a racemic mixture with equal amounts of both enantiomer (optically inactive).
The $S_N2$ mechanism is stereospecific – the backside attack by the nucleophile produces inversion of the configuration.

![Reaction Mechanism](image)

The inversion of the configuration produces only one enantiomer (optically active).
The $S_{N1}$ reaction produces a racemic mixture of the two enantiomers which is optically inactive. It has no effect on the plane of plane-polarised light.

The $S_{N2}$ reaction is stereospecific with inversion of the configuration – the product is optically active. It will rotate the plane of plane-polarised light.
Choice of solvent for $S_N^1/S_N^2$
Polar protic solvents contain O-H or N-H bonds and are able to form hydrogen bonds.

Polar aprotic solvents do not contain O-H or N-H bonds and are unable to form hydrogen bonds.
$S_N\text{1}$ reactions are favoured by the use of polar protic solvents.

The solvent molecules solvate the carbocation intermediate through ion-dipole interactions. This has the effect of stabilising the carbocation intermediate.

The solvent also stabilises the anion (the leaving group) by forming hydrogen bonds, which also favours $S_N\text{1}$ reactions.
$S_{N2}$ reactions are favoured by the use of polar aprotic solvents.

Polar aprotic solvents do not solvate the nucleophile, maintaining its reactivity – this favours the $S_{N2}$ reaction.

Polar protic solvents solvate the nucleophile (due to hydrogen bonding), reducing its reactivity.
Comparison of $S_{N1}$ and $S_{N2}$ reactions
# Nucleophilic Substitution Reactions

<table>
<thead>
<tr>
<th></th>
<th>$S_{N}1$</th>
<th>$S_{N}2$</th>
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<tbody>
<tr>
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<td><strong>Number of steps</strong></td>
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<td>One-step</td>
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<td><strong>Transition state or reaction intermediate</strong></td>
<td>Carbocation intermediate</td>
<td>Transition state</td>
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<td><strong>Type of solvent</strong></td>
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<td><strong>Type of bond fission</strong></td>
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<tr>
<td></td>
<td>$S_{N1}$</td>
<td>$S_{N2}$</td>
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<tr>
<td>----------------------</td>
<td>---------------------------------------</td>
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</tr>
<tr>
<td><strong>Molecularity</strong></td>
<td>Unimolecular</td>
<td>Bimolecular</td>
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<td><strong>Example rate</strong></td>
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<td>$rate = k[CH_3CH_2Br][OH^-]$</td>
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<tr>
<td><strong>Relative rate</strong></td>
<td>$3^\circ &gt; 2^\circ &gt; 1^\circ$</td>
<td>$1^\circ &gt; 2^\circ &gt; 3^\circ$</td>
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<td><strong>reaction</strong></td>
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<td><strong>Change in</strong></td>
<td>50/50 mix of enantiomers</td>
<td>Inversion of configuration</td>
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<tr>
<td><strong>stereochemistry</strong></td>
<td>(racemic mixture - optically inactive)</td>
<td>(optically active)</td>
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</tbody>
</table>
Nucleophilic substitution reactions

$S_{N1}$

$\text{CH}_3\text{C}^+\text{Br}^- \rightarrow \text{CH}_3\text{C}^+ + \text{Br}^-$

$\text{CH}_3\text{C}^+ \rightarrow \text{CH}_3\text{C}^-\text{OH}$

$S_{N2}$

$\text{H}_3\text{C}^+\text{Cl}^- \rightarrow \left[\text{HO}^\cdots\text{C}^+\text{Cl}\right]^- \rightarrow \text{HO}^\cdots\text{C}^-\text{H}_3\text{C} + \text{Cl}^-$

unstable transition state
Electrophilic addition reactions
The carbon to carbon double bond in an alkene has a region of high electron density above and below the plane of the molecule.

Because of this high electron density, the π bond is attractive to electrophiles (species that are electron deficient).

\[
\text{H}_2\text{C}==\text{C} + \text{H-Br} \rightarrow \text{H-} \text{C}==\text{C-H}
\]
The H-Br bond breaks heterolytically forming a bromide ion. At the same time, the H atom bonds to one of the C atoms forming a carbocation. The carbocation then combines with the Br\(^{-}\) ion forming bromoethane.
The bromine molecule breaks heterolytically forming $\text{Br}^+$ and $\text{Br}^-$. The $\text{Br}^+$ bonds to the one of the C atoms forming a carbocation intermediate. The carbocation then combines with the $\text{Br}^-$ forming 1,2-dibromoethane.
Electrophilic addition reactions

\[ \text{C}_2\text{H}_4 + \text{HBr} \rightarrow \text{CH}_3\text{CH}_2\text{Br} \]

\[ \text{C}_2\text{H}_4 + \text{Br}_2 \rightarrow \text{CH}_2\text{BrCH}_2\text{Br} \]
Markovnikov’s rule
Markovnikov’s rule can be used to predict the major product with a hydrogen halide reacts with an asymmetrical alkene.

\[
\text{H}_2\text{C}=\text{C}=\text{C}-\text{C}+\text{H}-\text{Cl} \rightarrow \text{H}-\text{C}=\text{C}-\text{C}-\text{C}-\text{H}
\]

1-chlorobutane

or

2-chlorobutane
When propene (an asymmetrical alkene) reacts with hydrogen bromide, there are two possible products:

1. 1-bromopropane
   \[
   \text{H}_3\text{C} \text{CH} = \text{CH}_2 + \text{HBr} \rightarrow \text{H}_3\text{C} - \text{C} \text{CH}_2 \text{Br}
   \]

2. 2-bromopropane
   \[
   \text{H}_3\text{C} \text{CH} = \text{CH}_2 + \text{HBr} \rightarrow \text{H}_3\text{C} - \text{C} - \text{C} \text{H}_2 \text{Br}
   \]
When an asymmetrical alkene reacts with a hydrogen halide, the hydrogen adds to the carbon atom that is already bonded to the greatest number of hydrogens.

\[
\begin{align*}
\text{H--C--C=C=CH}_2 + \text{HBr} & \rightarrow \text{H--C--C=C--H} \\
\text{H--C--C--C=C--H} + \text{HCl} & \rightarrow \text{H--C--C--C--C--H}
\end{align*}
\]
The primary carbocation is less stable than the secondary carbocation. The order of stability is: \(1^o < 2^o < 3^o\)

The major product will be 2-bromopropane because of the greater stability of the secondary carbocation.
Carbocations are stabilised by electron-donating alkyl groups (positive inductive effect). The more substituted the carbocation, the greater the stability.
When an asymmetrical alkene reacts with a hydrogen halide, the hydrogen adds to the carbon that is already bonded to the greatest number of hydrogens.
When an unsymmetrical alkene reacts with an interhalogen (I-Cl), the electrophilic portion of the molecule bonds to the carbon that is bonded to the greatest number of hydrogens.
Nitration of benzene
Benzene reacts with a mixture of concentrated nitric acid ($\text{HNO}_3$) and concentrated sulfuric acid ($\text{H}_2\text{SO}_4$) to form nitrobenzene ($\text{C}_6\text{H}_5\text{NO}_2$) and water.

The concentrated $\text{H}_2\text{SO}_4$ acts as a catalyst.

This is an electrophilic substitution reaction.
The mixture of concentrated nitric acid and concentrated sulfuric acid is known as a nitrating mixture. The sulfuric acid protonates the nitric acid, which then loses a molecule of water to form the nitronium ion (NO$_2^+$).
Nitration of benzene

$\text{NO}_2^+$ is a strong electrophile and is attracted to the delocalized $\pi$ electron cloud in benzene. It then reacts with the $\pi$ electrons to form a carbocation intermediate. The loss of a hydrogen ion (proton) leads to the reformation of the arene ring in the nitrobenzene. The hydrogen ion released reacts with the $\text{HSO}_4^-$ to reform the sulfuric acid catalyst.
NO$_2^+$ is a strong electrophile and is attracted to the delocalized $\pi$ electron cloud in benzene. It then reacts with the $\pi$ electrons to form a carbocation intermediate. The loss of a hydrogen ion (proton) leads to the reformation of the arene ring in the nitrobenzene. The hydrogen ion released reacts with the HSO$_4^-$ to reform the sulfuric acid catalyst.
Nitration of benzene

$$\text{C}_6\text{H}_6 + \text{HNO}_3 \xrightarrow{\text{H}_2\text{SO}_4 \text{ (conc.)}, 50^\circ\text{C}} \text{C}_6\text{H}_5\text{NO}_2 + \text{H}_2\text{O}$$
Reduction of carbonyl compounds
The carbon to oxygen bond is a polar bond because of the difference in electronegativity between carbon and oxygen.
Primary and secondary alcohols can be oxidized to aldehydes, ketones or carboxylic acids depending on the conditions.
These oxidation reactions can be reversed by using a suitable reducing agent. Sodium borohydride (NaBH$_4$), in aqueous or alcoholic solution (protic solvents). Lithium aluminium hydride (LiAlH$_4$) in anhydrous conditions such as dry ether (aprotic solvent). The reaction is then acidified to obtain the product. Both these reagents produce the hydride ion (H$^-$) which acts as a reducing agent undergoing a nucleophilic addition reaction with the electron deficient carbon atom of the carbonyl group.
Reduction reactions

aldehyde $\xrightarrow{1. \text{NaBH}_4} \xrightarrow{2. \text{H}^+_{\text{(aq)}}}$ primary alcohol

Conditions: heat with NaBH$_4$, then acidify.
Reduction reactions

ketone $\xrightarrow{1. \text{NaBH}_4}$ secondary alcohol $\xrightarrow{2. \text{H}^+_{(aq)}}$

Conditions: heat with $\text{NaBH}_4$, then acidify.
Conditions: heat with LiAlH\textsubscript{4} in dry ether, then acidify (NaBH\textsubscript{4} is not a strong enough reducing agent to reduce carboxylic acids).
Reduction of nitrobenzene
Nitrobenzene \((C_6H_5NO_2)\) can be reduced to phenylamine (aniline), \(C_6H_5NH_2\), in a two stage reaction.
Stage 1 – $\text{C}_6\text{H}_5\text{NO}_2$ is reacted with Sn and conc. HCl (heat under reflux in a boiling water bath). The product is the phenylammonium ion ($\text{C}_6\text{H}_5\text{NH}_3^+$)

$$\text{C}_6\text{H}_5\text{NO}_2(\text{l}) + 3\text{Sn}(\text{s}) + 7\text{H}^+(\text{aq}) \rightarrow \text{C}_6\text{H}_5\text{NH}_3^+(\text{aq}) + 3\text{Sn}^{2+}(\text{aq}) + 2\text{H}_2\text{O}(\text{l})$$
Stage 2 – $\text{C}_6\text{H}_5\text{NH}_3^+$ is reacted with NaOH to remove the hydrogen ion ($\text{H}^+$) and produce phenylamine ($\text{C}_6\text{H}_5\text{NH}_2$).

$$\text{C}_6\text{H}_5\text{NH}_3^+ (\text{aq}) + \text{OH}^- (\text{aq}) \rightarrow \text{C}_6\text{H}_5\text{NH}_2 (\text{l}) + \text{H}_2\text{O} (\text{l})$$
Nitrobenzene ($C_6H_5NO_2$) can be reduced to phenylamine (aniline) ($C_6H_5NH_2$) in a two stage reaction.

Stage 1 – $C_6H_5NO_2$ is reacted with Sn and concentrated HCl (heat under reflux in a boiling water bath).

The product is the phenylammonium ion ($C_6H_5NH_3^+$)

$$C_6H_5NO_2 (l) + 3Sn (s) + 7H^+ (aq) \rightarrow C_6H_5NH_3^+ (aq) + 3Sn^{2+} (aq) + 2H_2O (l)$$
MSJChem
Tutorials for IB Chemistry

Retro-synthesis
Outline the steps involved in the retro-synthesis of butanone starting with an alkene.

\[
\text{CH}_3\text{COCH}_2\text{CH}_3 \rightarrow \text{CH}_3\text{CH(OH)}\text{CH}_2\text{CH}_3 \quad \text{(oxidation H}^+\text{/Cr}_2\text{O}_7^{2-})
\]

butanone    butan-2-ol

\[
\text{CH}_3\text{CH}_2(\text{OH})\text{CH}_2\text{CH}_3 \rightarrow \text{CH}_3\text{CH(}\text{Br})\text{CH}_2\text{CH}_3 \quad (\text{S}_\text{N1}/\text{S}_\text{N2} \text{ NaOH})
\]

butan-2-ol    2-bromobutane

\[
\text{CH}_3\text{CH}_2(\text{Br})\text{CH}_2\text{CH}_3 \rightarrow \text{CH}_2\text{CHCH}_2\text{CH}_3 \quad \text{(addition HBr)}
\]

2-bromobutane    but-2-ene
Retro-synthesis involves planning a synthesis backwards, by starting at the product, (the target molecule) and taking it back one step at a time to simple, available starting materials (precursors).

target molecule $\Rightarrow$ precursor 1 $\Rightarrow$ precursor 2 $\Rightarrow$ starting material
Organic reaction pathways
Isomerism
Isomerism

Isomerism – compounds with same molecular formula but different arrangement of atoms

Stereoisomerism – different spatial arrangement of atoms

Structural isomerism – atoms and functional groups attached in different ways
Isomerism

Stereoisomerism

- Configurational isomerism – interconvert only by breaking a bond
- Conformational isomerism – interconvert by rotation around a σ bond
Isomerism

Configurational isomerism

- cis-trans and E/Z isomerism – restricted rotation around atoms
- Optical isomerism – asymmetric or chiral carbon atom
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Conformational isomerism
Conformational isomers (conformers) are stereoisomers produced by rotation about carbon-carbon single bonds.

C=C bond made of 1 σ and 1 π bond (restricted rotation)

C-C bond made of 1 σ bond (free rotation)

The two conformers can interconvert readily at room temperature.
Conformational isomers

Eclipsed conformer

Staggered conformer
The staggered conformation is more stable by approximately 12 kJ mol\(^{-1}\).
Conformational isomers occur because of the free rotation around a carbon-carbon single bond (composed of one σ bond). The staggered conformers are more stable than the eclipsed conformers. The two conformers interconvert rapidly at room temperature because of the small difference in energy between them.
MSJChem
Tutorials for IB Chemistry
cis-trans isomerism
cis-trans isomerism occurs where there is restricted rotation around a carbon to carbon bond.

Restricted rotation around a C=C bond

Restricted rotation in a cyclic compound
For *cis-trans* isomerism to occur, there must be two different groups on each of the carbon atoms of the C=C bond.

This molecule does not have *cis-trans* isomers

This molecule does have *cis-trans* isomers
The π bond in the C=C bond restricts rotation, forming two different isomers.

**cis** isomer – same groups on the same side of C=C bond.

**trans** isomer – same groups on opposite sides of C=C bond.
*cis*-trans isomerism

**cis-but-2-ene**

**trans-but-2-ene**
Cyclic compounds contain a ring structure that restricts rotation. When the molecule contains two or more different substituents attached to the ring, two different isomers are formed.

* cis isomer has the substituents on the same side of the ring, trans isomer has the substituents on opposite sides of the ring.*

\[ \text{cis-1,3-dichlorocyclobutane} \quad \text{trans-1,3-dichlorocyclobutane} \]
cis-trans isomerism

cis-pent-2-ene

trans-pent-2-ene

cis-1,2-dibromocyclobutane

trans-1,2-dibromocyclobutane
Physical properties of *cis*-trans isomers
The polarity of the molecule influences the boiling point.
The symmetry of the molecule influences the melting point (closely packed molecules have stronger intermolecular forces).
The cis-isomer forms intramolecular hydrogen bonds (within the molecule). The trans-isomer forms intermolecular hydrogen bonds (between molecules).
E/Z isomerism
E/Z notation is used when there are up to four different substituents bonded to the two carbon atoms of the C=C bond.

- cis-but-2-ene

\[
\begin{align*}
\text{cis-}: & \quad \text{H} \quad \text{H} \\
\text{but-2-ene:} & \quad \text{CH}_3 \quad \text{CH}_3 \\
\text{C} & \quad \text{C} \\
\text{=} & \quad \text{=} \\
\text{C} & \quad \text{C} \\
\text{=} & \quad \text{=} \\
& \quad \text{H} \\
\end{align*}
\]
E/Z isomerism is based on the Cahn-Ingold-Prelog (CIP) rules of priority which assign priority to each atom or group of atoms around the C=C bond.

\[
\begin{align*}
\text{H } Z &= 1 \\
\text{Br } Z &= 35 \\
\text{C-H } Z &= 1 \\
\text{C-C } Z &= 6
\end{align*}
\]
If the highest priority groups are on the same side of the C=C, it is the Z isomer. If the highest priority groups are on opposite sides of the C=C, it is the E isomer.
E/Z isomerism

(Z)-1-bromo-1-chloro-2-iodo-1-propene

(E)-1-bromo-1-chloro-2-iodo-1-propene

(E)-1-bromo-2-chloro-1-iodoethene

(Z)-1-bromo-2-chloro-1-iodoethene
How to determine if the isomer is $E$ or $Z$:

1. Assign priority to the atoms or groups of atoms on each carbon atom of the C=C double bond
   
   \[ I > Br > Cl > F \]

   \[ C_3H_7 > C_2H_5 > CH_3 \]

2. If the highest priority groups are on the same side of the C=C bond, it is the $Z$ isomer (together).

3. If the highest priority groups are on opposite sides of the C=C bond, it is the $E$ isomer (opposite).
Optical isomerism
Optical isomerism is shown by chiral molecules that have a carbon atom bonded to four different atoms or groups (chiral center or asymmetric carbon).
The four groups can be arranged in two three-dimensional configurations which are mirror images of each other. The two mirror images are non-superimposable and are known as enantiomers.
Optical isomerism
Optical isomerism
The two optical isomers (enantiomers) are optically active with plane-polarised light.
Optical isomerism

mirror
Enantiomers have identical physical properties, such as melting point and boiling point, except that they rotate the plane of plane-polarised light in opposite directions (optically active). This property is used to distinguish between the two enantiomers of a chiral molecule. The chemical properties of two enantiomers are also identical, except when they react with other chiral molecules (such as those found in the human body).
How to distinguish between enantiomers of a chiral compound
Ordinary light consists of waves that vibrate in all planes perpendicular to its direction of travel. Plane-polarised light consists of waves vibrating in one plane only.
The two enantiomers of a chiral compound rotate the plane of plane-polarised light by the same angle but in opposite directions.

- **Enantiomer A**: 20° clockwise rotation
- **Enantiomer B**: 20° anti-clockwise rotation
Plane-polarised light is passed through a tube containing a solution of the enantiomer. The plane of the plane-polarised light is rotated which then passes through the analyser. The analyser is rotated until the light passes through and the angle and direction of rotation can be measured.
A solution containing equal amounts of both enantiomers is known as a racemic mixture (racemate). If both enantiomers are present in equal amounts, the two rotations cancel out and the mixture is said to be optically inactive.

![Diagram](image-url)

- Plane-polarised light
- 20° clockwise rotation
- 20° anti-clockwise rotation
- No overall rotation
When chiral compounds are made in the laboratory, they often occur as a 50/50 mixture of the two enantiomers, which is optically inactive (no effect on plane-polarised light). Biological processes within cells produce only one form of the enantiomer and are therefore optically active (rotate the plane of plane-polarised light).
Diastereomers
Enantiomers are stereoisomers that are mirror images of one another and are non-superimposable.
Diastereomers are stereoisomers that are not mirror images of one another and are non-superimposable.

2,3,4-trihydroxybutanal
Diastereomers

The number of possible optical isomers for a chiral molecule is $2^n$, where $n$ is the number of chiral centres in the molecule.

2-chlorobutane

2,3,4-trihydroxybutanal
A and B are enantiomers  
C and D are enantiomers

Enantiomers are mirror images and non-superimposable. They have opposite configurations at all chiral centres.
Diastereomers are not mirror images and are non-superimposable. They have opposite configurations at some, but not all of the chiral centres.

<table>
<thead>
<tr>
<th>A</th>
<th>CHO</th>
<th>C</th>
<th>CHO</th>
<th>B</th>
<th>CHO</th>
<th>D</th>
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A and C are diastereomers
B and D are diastereomers
<table>
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<tr>
<th>Enantiomers</th>
<th>Diastereomers</th>
</tr>
</thead>
<tbody>
<tr>
<td>Are mirror images and are non-superimposable</td>
<td>Are not mirror images and are non-superimposable</td>
</tr>
<tr>
<td>Have one or more chiral centres</td>
<td>Have at least two chiral centres</td>
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<tr>
<td>Have opposite configurations at all chiral centres</td>
<td>Have opposite configurations at some, but not all chiral centres</td>
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<tr>
<td>Have the same physical and chemical properties</td>
<td>Have different physical and chemical properties</td>
</tr>
<tr>
<td>Are optically active</td>
<td>Not all diastereomers are optically active</td>
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