DP IB Chemistry: HL

Your notes

20.1 Types of Organic Reactions

Contents

20.1.1 Nucleophilic Substitution Reactions

Nucleophilic Substitution Reactions

- In nucleophilic substitution reactions involving halogenoalkanes, the halogen atom is replaced by a nucleophile
- The strength of any nucleophile depends on its ability to make its lone pair of electrons available for reaction
- The hydroxide ion, OH^-, is a stronger nucleophile than water because it has a full negative charge
    - This means that it has a readily available lone pair of electrons
- A water molecule only has partial charges, δ+ and δ-
    - This means that its lone pair of electrons is less available than the hydroxide ions
    - The lone pairs of electrons in a water molecule are still available to react

Lewis structures of the hydroxide ion and water molecule - illustrating the lone pairs of electrons and charges within their structures

Examiner Tip

In general:

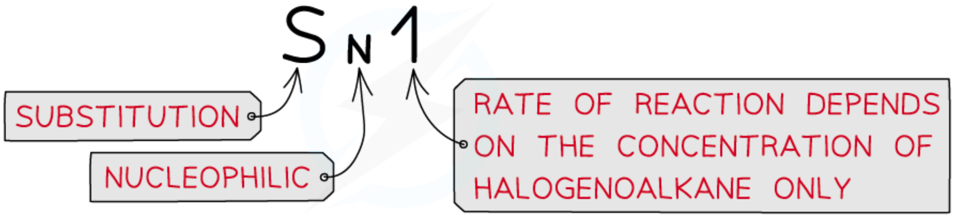
- A negatively charged ion will be a stronger nucleophile than a neutral molecule
- A conjugate base will be a stronger nucleophile than its corresponding conjugate acid
    - e.g. the hydroxide ion is a stronger nucleophile than water

SN1 Mechanism

- Nucleophilic substitution reactions can occur in two different ways (known as **S_N2** and **S_N1** reactions) depending on the structure of the halogenoalkane involved

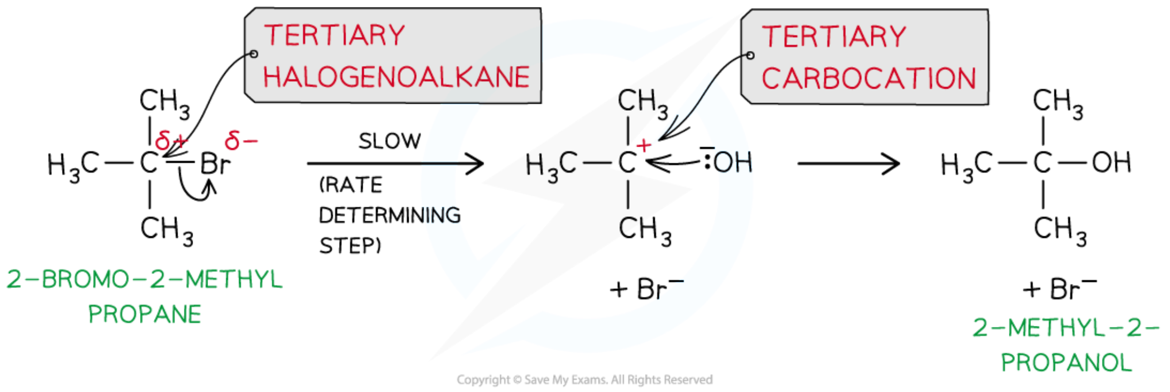
S_N1 reactions

- In **tertiary** halogenoalkanes, the carbon that is attached to the halogen is also bonded to three alkyl groups
- These halogenoalkanes undergo nucleophilic substitution by an **S_N1** mechanism
  - 'S' stands for 'substitution'
  - 'N' stands for 'nucleophilic'
  - '1' means that the rate of the reaction (which is determined by the slowest step of the reaction) depends on the concentration of only one reagent, the halogenoalkane



- 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 is the **slow** and **rate-determining step**)
  - As the rate-determining step only depends on the concentration of the halogenoalkane, the rate equation for an S_N1 reaction is **rate = *k*[halogenoalkane]**
  - In terms of molecularity, an S_N1 reaction is unimolecular
  - This forms a tertiary carbocation (which is a tertiary carbon atom with a positive charge)
  - In the second step, the tertiary carbocation is attacked by the nucleophile

- For example, the nucleophilic substitution of 2-bromo-2-methylpropane by hydroxide ions to form 2-methyl-2-propanol



The mechanism of nucleophilic substitution in 2-bromo-2-methylpropane which is a tertiary halogenoalkane

Examiner Tip

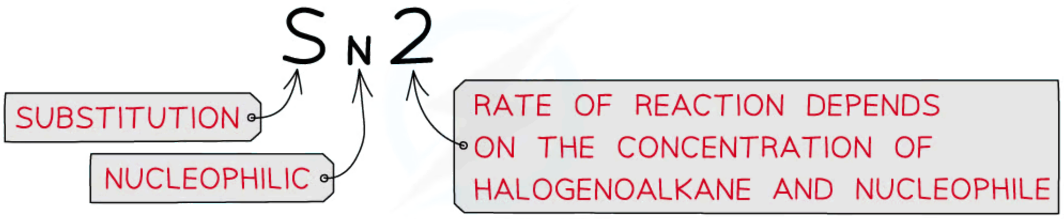
You are expected to know the difference between the heterolytic fission that features in S_N1 reactions and homolytic fission in other reactions:

- Heterolytic fission forms anions and cations and uses double headed arrows to show the movement of both electrons from the covalent bond
- Homolytic fission forms free radicals and uses single headed arrows, sometimes called fish hooks, to show the movement of a single electron as the covalent bond breaks

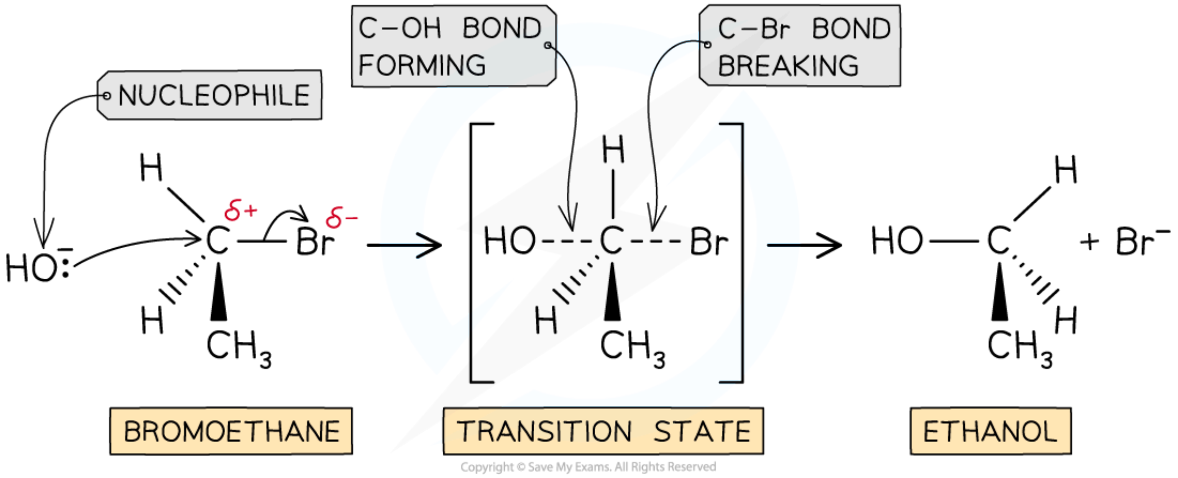
SN2 Mechanism

S_N2 reactions

- In **primary** halogenoalkanes**,** the carbon that is attached to the halogen is bonded to one alkyl group
- These halogenoalkanes undergo nucleophilic substitution by an **S_N2** mechanism
  - 'S' stands for 'substitution'
  - 'N' stands for 'nucleophilic'
  - '2' means that the rate of the reaction (which is determined by the slowest step of the reaction) depends on the concentration of both the halogenoalkane and the nucleophile ions

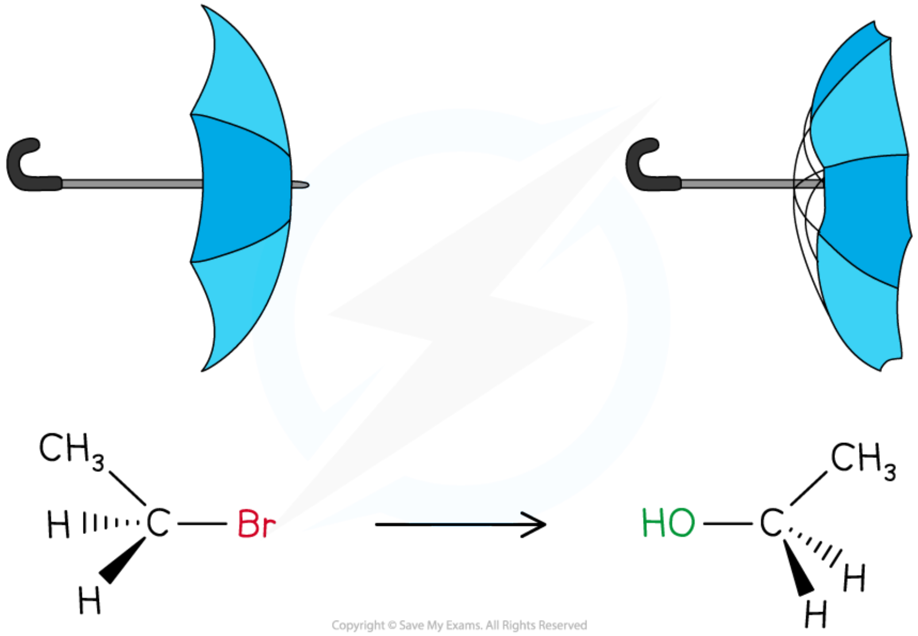


- The S_N2 mechanism is a **one-step** reaction
  - The nucleophile donates a pair of electrons to the δ+ carbon atom of the halogenoalkane to form a new bond
    - As this is a one-step reaction, the rate-determining step depends on the concentrations of the halogenoalkane and nucleophile, the rate equation for an S_N2 reaction is **rate = *k*[halogenoalkane][nucleophile]**
    - In terms of molecularity, an S_N2 reaction is bimolecular
  - At the same time, the C-X bond is breaking and the halogen (X) takes both electrons in the bond (heterolytic fission)
  - 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

Examiner Tip

If you are asked to explain reaction mechanisms where there is an inversion of configuration, you will be expected to:

- Use partial charges, δ+ and δ-, to help explain why the nucleophile attacks and the halogen leaves
- Use dotted, wedge and tapered bonds to show the change in configuration of the atoms / functional groups around the carbon that is being attacked
- Draw the transition state with the nucleophile attached to the carbon with a dotted bond and the halogen still attached to the carbon, also, with a dotted bond
- Be aware that the compound you draw is a transition state and not an intermediate

Factors Affecting Nucleophilic Substitution

Factors affecting nucleophilic substitution

- Various factors affect the rate of nucleophilic substitution, regardless of S_N1 or S_N2, involving a halogenoalkane:

  1. The nature of the nucleophile
  2. The halogen involved (leaving group)
  3. The structure (class) of the halogenoalkane
  4. Protic & aprotic solvents

1. The nature of the nucleophile

- The most effective nucleophiles are neutral or negatively charged species that have a lone pair of electrons available to donate to the δ+ carbon in the halogenoalkane
- The greater the electron density on the nucleophile ion or molecule; the stronger the nucleophile
  - Consequently, negative anions tend to be more reactive than their corresponding neutral species, e.g. hydroxide ions and water molecules (as previously discussed)

- When nucleophiles have the same charge, the electronegativity of the atom carrying the lone pair becomes the deciding factor
  - The less electronegative the atom carrying the lone pair; the stronger the nucleophile
  - For example:
    - Ammonia is a stronger nucleophile than water because the nitrogen atom in ammonia is less electronegative than the oxygen atom in water

  - This is because a less electronegative atom has a weaker grip on its lone pair of electrons, which means that they are more available for reaction

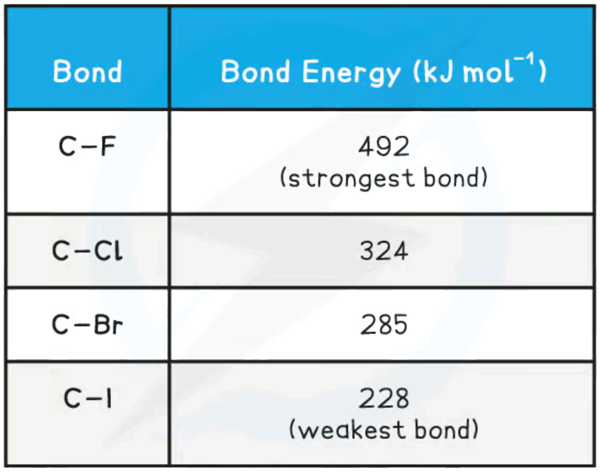
- The effectiveness of nucleophiles is as follows:

Strongest $CN^- > OH^- > NH_3 > H_2O$ Weakest

2. The halogen involved (leaving group)

- The halogenoalkanes have different rates of substitution reactions
- Since substitution reactions involve breaking the carbon-halogen bond, the bond energies can be used to explain their different reactivities

Approximate Halogenoalkane Bond Energy Table



Bond	Bond Energy (kJ mol^{-1})
C−F	492 (strongest bond)
C−Cl	324
C−Br	285
C−I	228 (weakest bond)

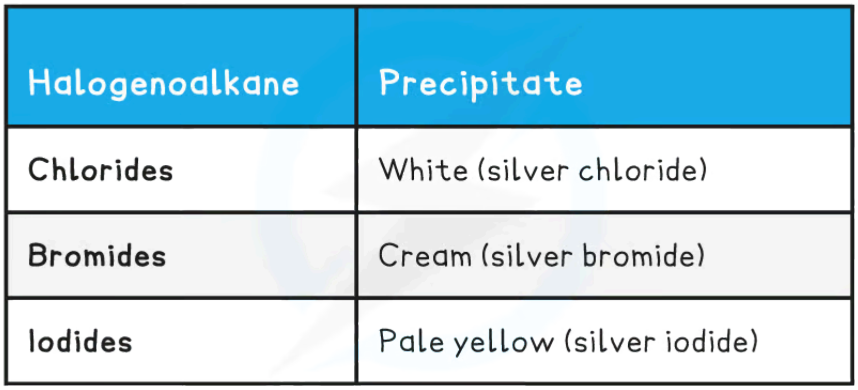
- The table above shows that the C-I bond requires the least energy to break, and is therefore the weakest carbon-halogen bond
    - During substitution reactions, the C-I bond will breaks heterolytically as follows:

$$R_3C\text{-}I + OH^- \rightarrow R_3C\text{-}OH + I^-$$

- The C-F bond, on the other hand, requires the most energy to break and is, therefore, the strongest carbon-halogen bond
    - Fluoroalkanes will therefore be less likely to undergo substitution reactions

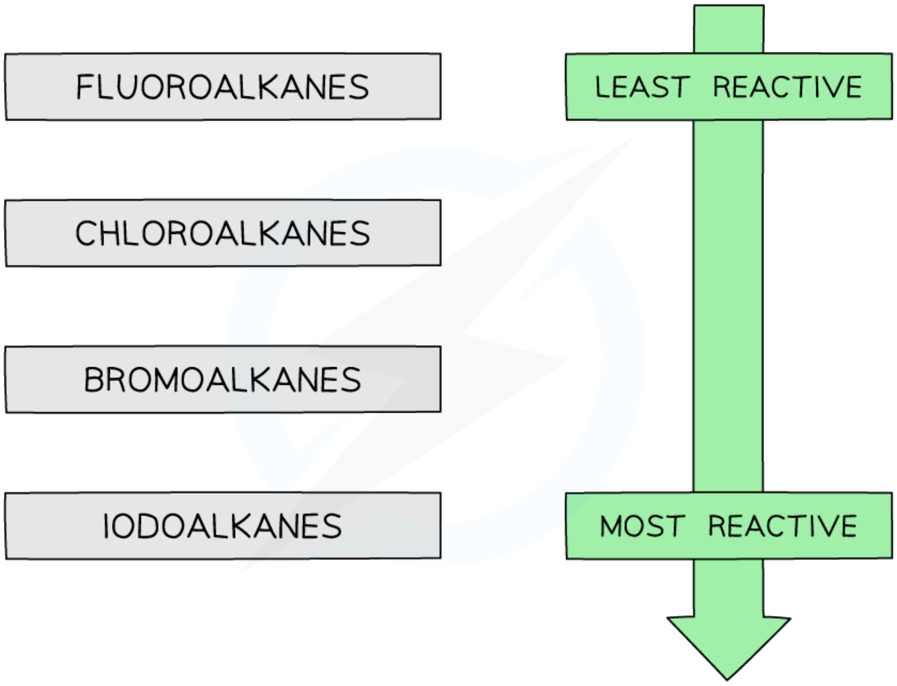
- This idea can be confirmed by reacting the product formed by nucleophilic substitution of the halogenoalkane with aqueous silver nitrate solution
- As a halide ion is released, this results in the formation of a precipitate
- The rate of formation of these precipitates can also be used to determine the reactivity of the halogenoalkanes

Halogenoalkane Precipitates Table



Halogenoalkane	Precipitate
Chlorides	White (silver chloride)
Bromides	Cream (silver bromide)
Iodides	Pale yellow (silver iodide)

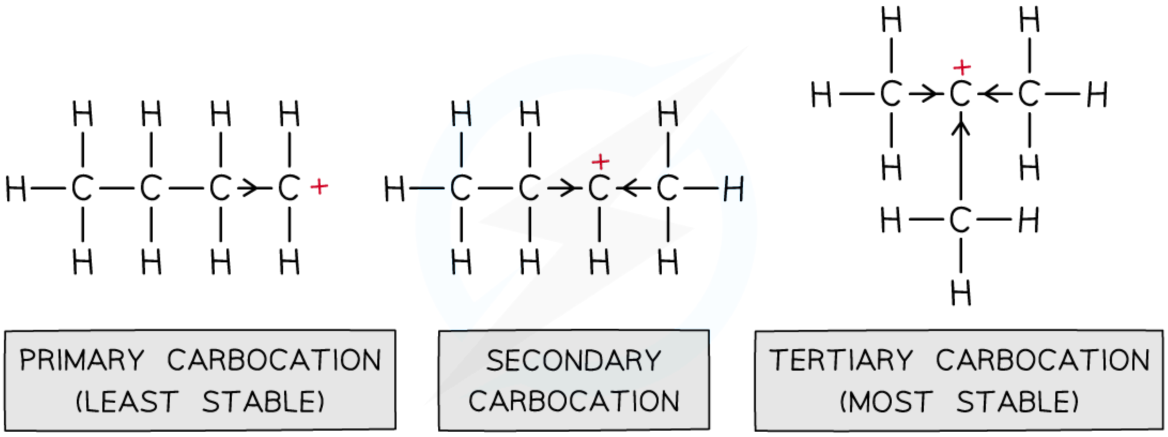
- The formation of the pale yellow silver iodide is the fastest (fastest nucleophilic substitution reaction) whereas the formation of the silver fluoride is the slowest (slowest nucleophilic substitution reaction)
- This confirms that fluoroalkanes are the least reactive and iodoalkanes are the most reactive halogenoalkanes



The trend in reactivity of halogenoalkanes

3. The structure (class) of the halogenoalkane

- Tertiary halogenoalkanes undergo S_N1 reactions, forming stable tertiary carbocations
- Secondary halogenoalkanes undergo a mixture of both S_N1 and S_N2 reactions depending on their structure
- Primary halogenoalkanes undergo S_N2 reactions, forming the less stable primary carbocations
- This has to do with the **positive inductive effect** of the alkyl groups attached to the carbon which is bonded to the halogen atom
  - The alkyl groups push electron density towards the positively charged carbon, reducing the charge density
  - In tertiary carbocations, there are three alkyl groups stabilising the carbocation
  - In primary carbocations, there is only one alkyl group
    - This is why tertiary carbocations are much more stable than primary ones



The diagram shows the trend in stability of primary, secondary and tertiary carbocations

- Overall, the structure (class) has a direct effect on the formation of the carbocation and, therefore, the rate-determining step
- Consequently, this affects the overall rate of the nucleophilic substitution reaction

Protic & Aprotic Solvents

4. Protic & Aprotic Solvents

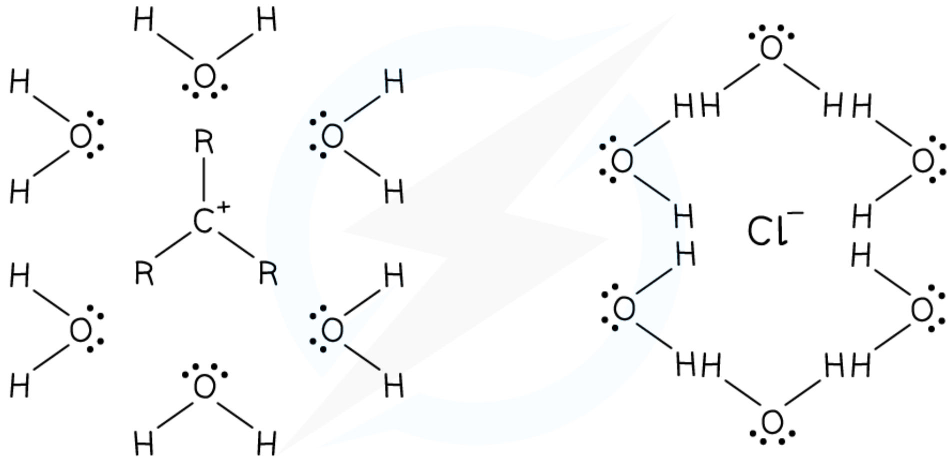
Hydrogen bonding

- Protic, polar solvents contain a hydrogen atom bonded to a very electronegative nitrogen or oxygen atom
    - This means that they are capable of hydrogen bonding
    - Examples of protic solvents include ammonia, carboxylic acids, ethanol and water

- Aprotic, polar solvents contain hydrogen atoms but they are not bonded to an electronegative atom
    - This means that they cannot participate in hydrogen bonding
    - Examples of aprotic solvents include ethanenitrile, ethyl ethanoate and propanone

Solvation

- Solvation is where solvent molecules surround a dissolved ion
    - In S_N1 reactions, the rate-determining step is **not** the attack of the nucleophile
    - The rate-determining step is the formation of the carbocation intermediates and halide ion
    - Both ions could be stabilised by the use of a protic solvent, as shown in the following example:



Protic polar solvent stabilising carbocation intermediates and halide ions

- In S_N2 reactions, the rate-determining step is the attack of the nucleophile
- The use of aprotic solvents does not **solvate** the nucleophile
- This means that the nucleophile is more able to react and form the transition state

- S_N1 reactions are best conducted using protic, polar solvents
- S_N2 reactions are best conducted using aprotic, polar solvents

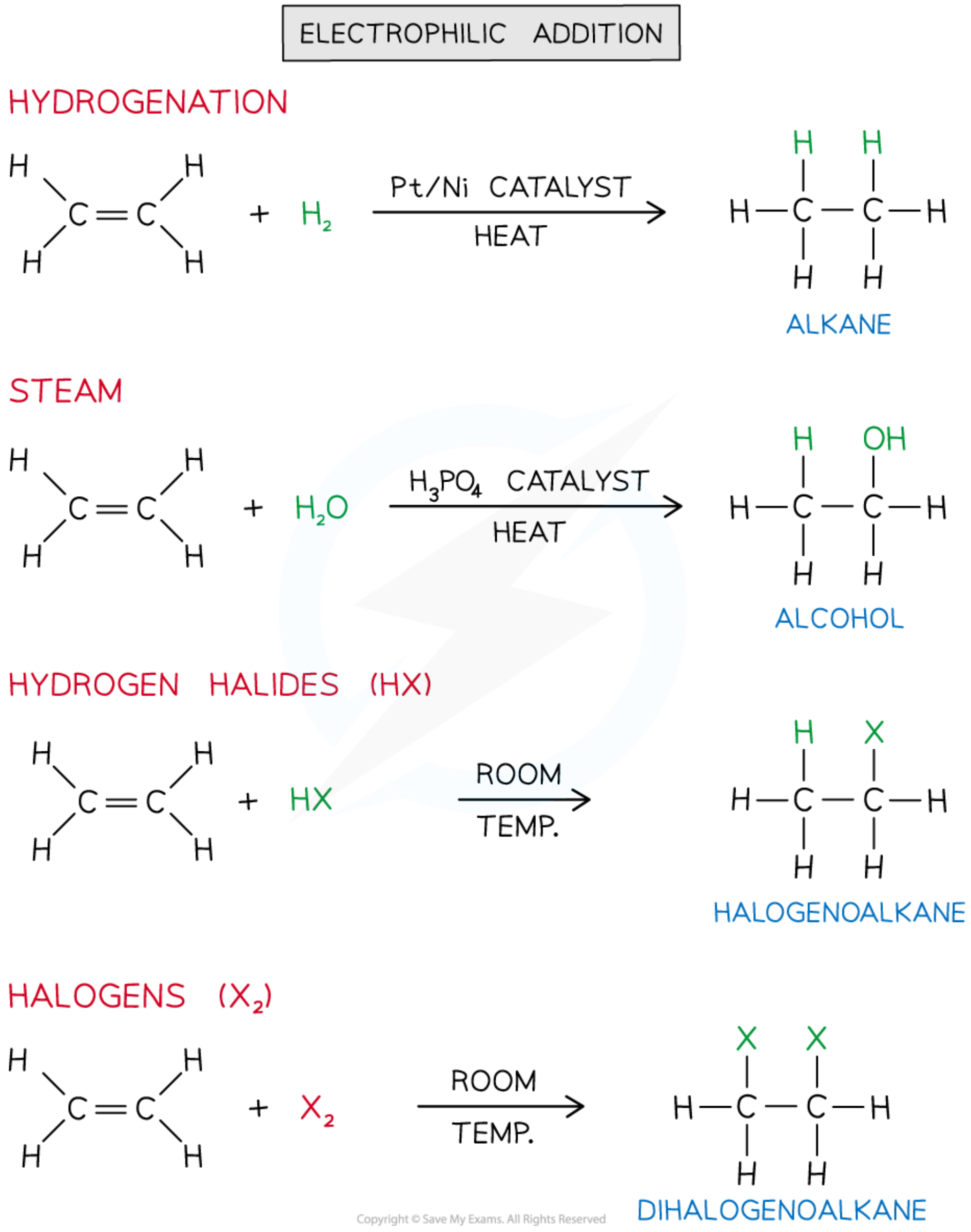
20.1.2 Electrophilic Addition Reactions

Your notes

Electrophilic Addition Mechanism

Electrophilic Addition

- **Electrophilic addition** is the addition of an electrophile (or Lewis acid) to an alkene double bond, C=C
- The alkene double bond, C=C, is an area of high electron density which makes it susceptible to attack by electrophiles
- The C=C bond breaks forming a single C-C bond and 2 new bonds from each of the two carbon atoms
- Electrophilic addition reactions include the addition of:
  - Hydrogen, H_2 (g)
  - Steam, H_2O (g)
  - Hydrogen halides, HX
  - Halogens, X_2

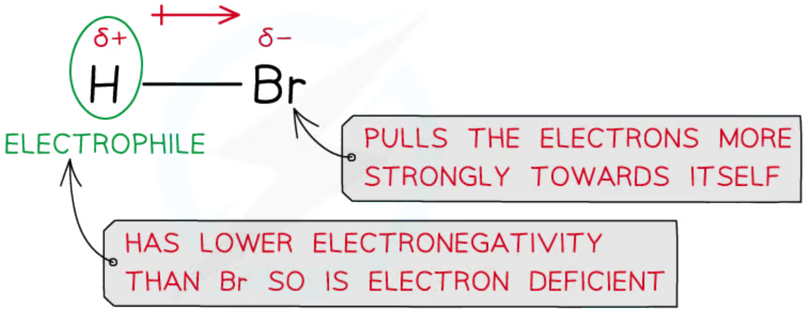


Alkene electrophilic addition reaction overview

Electrophilic addition of hydrogen halides

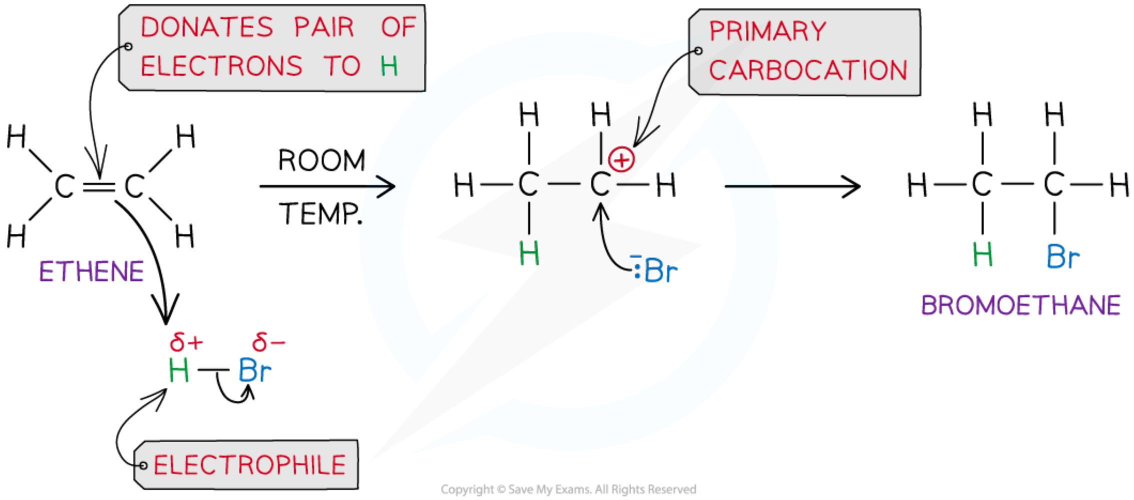
- A hydrogen halide molecule is polar as the hydrogen and halogen atoms have different electronegativities

- For example, in a molecule of hydrogen bromide, HBr, the bromine atom has a stronger pull on the electrons in the H-Br bond
- As a result of this, the Br atom has a partial negative and the H atom a partial positive charge



Due to differences in electronegativities of the hydrogen and bromine atom, HBr is a polar molecule

- In electrophilic addition reactions with hydrogen halides, the H atom acts as an electrophile and Lewis acid by accepting a pair of electrons from the C=C bond in the alkene
  - The H-Br bond breaks heterolytically, forming a Br^- ion
- This results in the formation of a highly reactive carbocation intermediate which reacts with the bromide ion, Br^-
- For example, the mechanism for the electrophilic addition of hydrogen bromide and ethene is:



Electrophilic addition reaction of HBr and ethene to form bromoethane

Examiner Tip

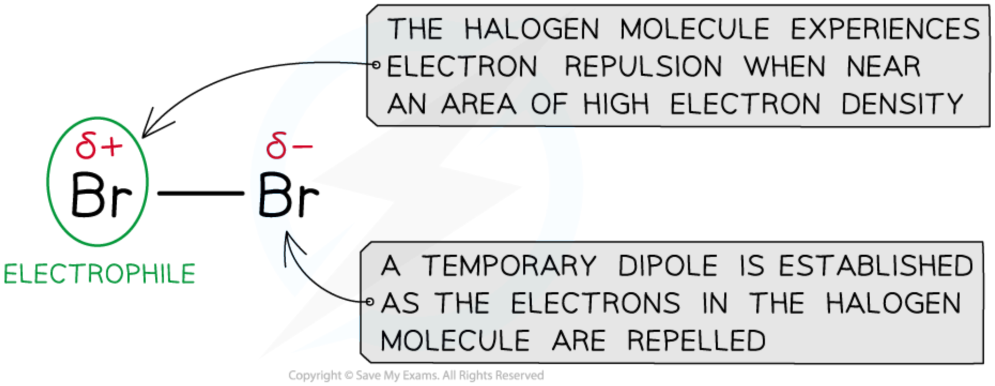
For electrophilic addition mechanisms, the curly arrows must:

- Be double-headed to show the movement of a pair of electrons
- Start from a lone pair of electrons or an area of high electron density, e.g. the C=C bond
- Move towards a δ+ electrophile or the positive charge of a carbocation

Examiners often comment about the poor and incorrect use of curly arrows in organic mechanisms

Electrophilic addition of halogens

- The mechanism for the electrophilic addition of halogens (and hydrogen) is the same as the electrophilic addition of hydrogen halides with one key exception:
  - Hydrogen halide molecules have a **permanent dipole** (as shown above)
  - Halogen molecules have a **temporary (or induced) dipole** caused by the repulsion of the halogens electrons by the high electron density C=C bond



The temporary (or induced) dipole in a halogen molecule

Electrophilic addition of interhalogens

- **Interhalogens** are compounds that contain two or more different type of halogens
- The mechanism for the electrophilic addition of interhalogens is the same as the electrophilic addition of hydrogen halides
- Just like hydrogen halide molecules, interhalogens have a **permanent dipole**
- Differences between the electronegativity of the halogens determine which halogen will become the δ+ electrophile
  - The electronegativity increases as you move up the halogens, F > Cl > Br > I

Your notes

The polarity of interhalogen molecules

Examiner Tip

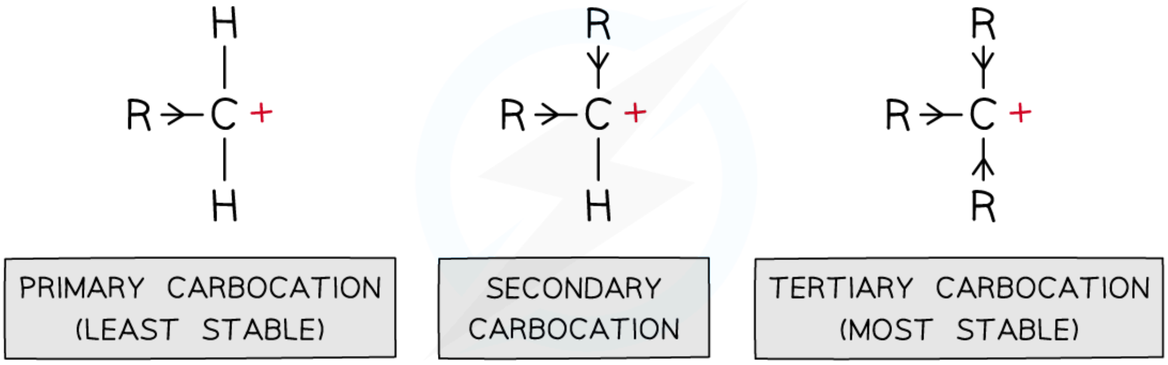
The electrophilic addition reactions of alkenes with hydrogen halides, halogens and interhalogens are the same. The difference is whether the electrophile is due to a permanent or temporary dipole

Markovnikov's Rule

- **Carbocations** are positively charged carbon atoms with only three covalent bonds instead of four
- There are three types of carbocations: primary, secondary and tertiary

Inductive effect

- The alkyl groups attached to the positively charged carbon atoms are 'electron donating groups'
  - This is also known as the inductive effect of alkyl groups
- The inductive effect is illustrated by the use of arrowheads on the bonds to show the alkyl groups pushing electrons towards the positively charged carbon
  - This causes the carbocation to become less positively charged
- As a result of this, the charge is spread around the carbocation which makes it energetically more stable
- This means that tertiary carbocations are the most stable as they have three electron-donating alkyl groups which energetically stabilise the carbocation
- Due to the positive charge on the carbon atom, carbocations are electrophiles



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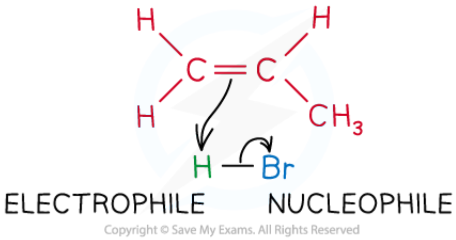
Alkyl groups push electron density towards the carbocation making it energetically more stable; the more alkyl groups the carbocation is bonded to, the more stabilised it is

Markovnikov's rule

- Markovnikov's rule predicts the outcome of electrophilic addition reactions and states that:
  - In an electrophilic addition reaction of a hydrogen halide (HX) to an alkene, the halogen ends up bonded to the most substituted carbon atom
  - In an electrophilic addition reaction of an interhalogen to an alkene, the most electronegative halogen ends up bonded to the most substituted carbon atom
- Markovnikov addition applies to electrophilic addition reactions with unsymmetrical alkanes, e.g. propene and but-1-ene

  - Markovnikov addition favours the formation of the major product
  - Anti-Markovnikov addition favours the formation of the minor product

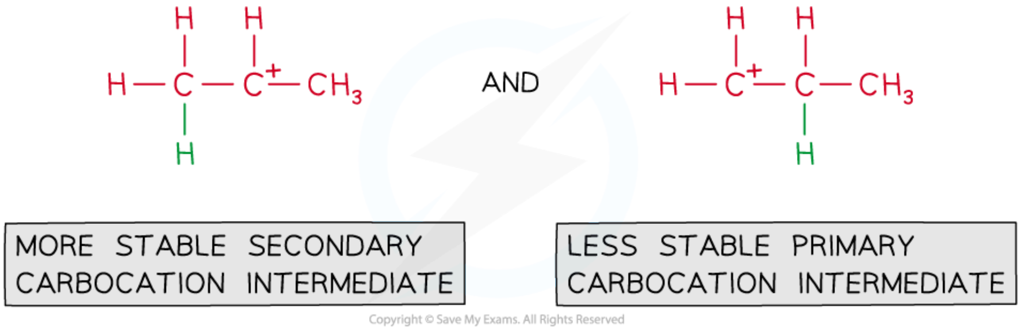
- In electrophilic addition reactions, an electrophile reacts with the double bond of alkenes (as previously discussed)
- The mechanism for electrophilic addition reactions with unsymmetrical alkenes is slightly different, e.g. propene + hydrogen bromide



The electrophile reacts with the electron-rich C-C double bond

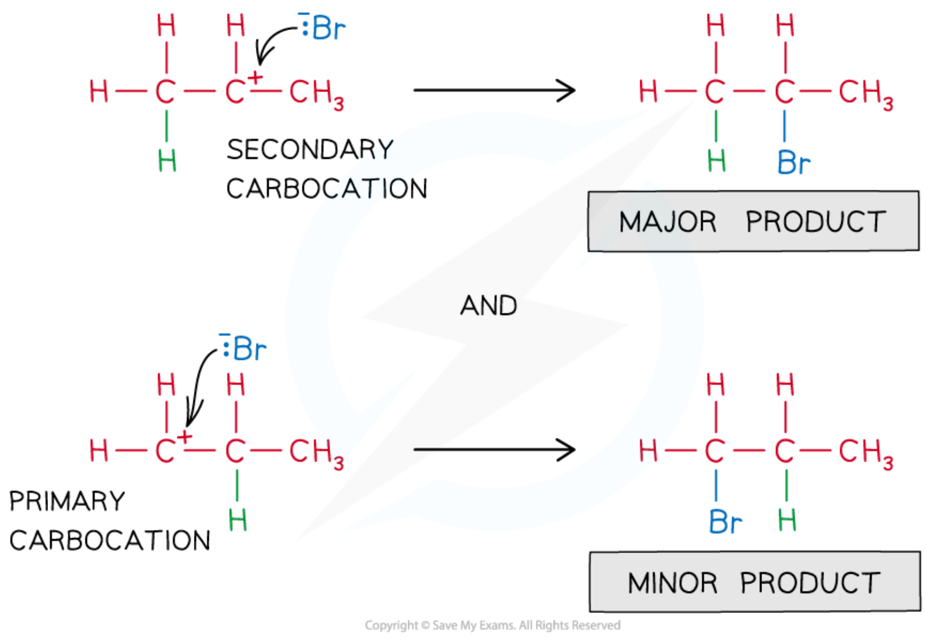
- The electrophile can attach in two possible ways:

1. Breaking the C=C bond and attaching to the the least substituted carbon
   - This will give the **most** stable carbocation as an intermediate that will form the **major** product
2. Breaking the C=C bond and attaching to the the most substituted carbon
   - This will give the **least** stable carbocation as an intermediate that will form the **minor** product



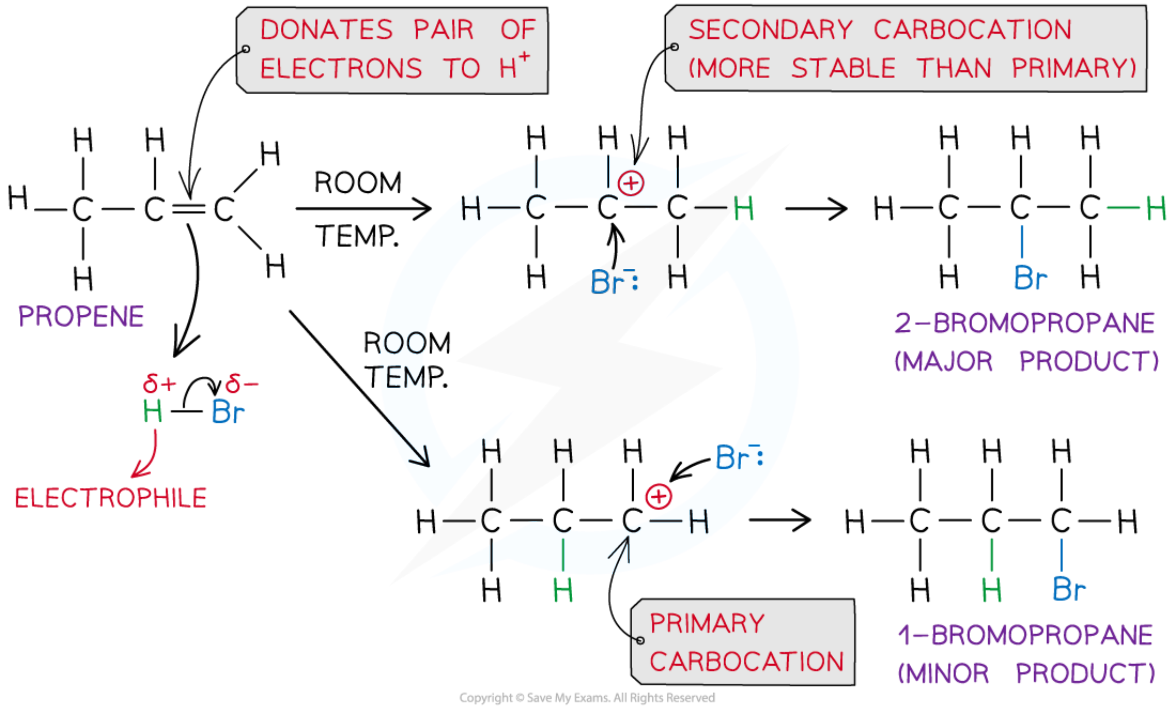
The major and minor carbocation intermediates formed during the reaction of propene and hydrogen bromide

- The nucleophile will bond to the positive carbon atom of the carbocation
  - The more stable carbocation produces the major product
  - The less stable carbocation produces the minor product



Formation of the major and minor products of the reaction of propene with hydrogen bromide

- The mechanism for the electrophilic addition of hydrogen bromide to propene, showing the formation of the major and minor products can be shown as:



The electrophilic addition reaction mechanism of HBr and propene to form 1-bromopropane and 2-bromopropane

Examiner Tip

The stability of the carbocation intermediate is as follows:

tertiary > secondary > primary

When more than one carbocation can be formed, the major product of the reaction will be the one that results from the nucleophilic attack of the most stable carbocation.

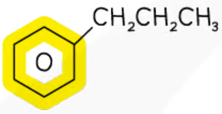
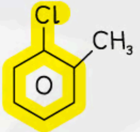
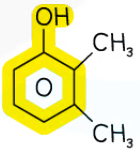
20.1.3 Electrophilic Substitution Reactions

The Structure of Benzene

- In normal, everyday conversation the word 'aromatic' is used to refer to pleasant, fragrant smells
- However, in chemistry, it is used to describe molecules that contain one or more benzene rings, i.e. a ring with **conjugated π systems**
    - Conjugated π systems arise from alternating double and single bonds in which the electrons are delocalised

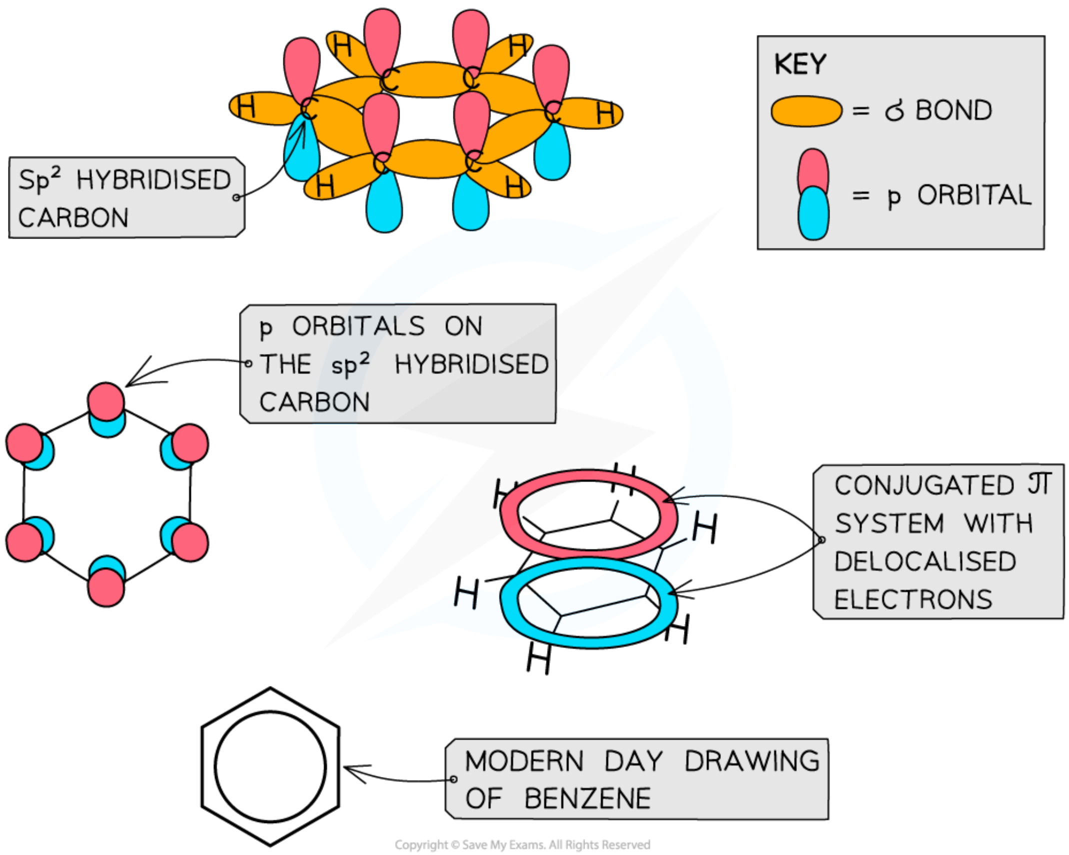
- Benzene is found in many useful pharmaceuticals, pesticides, polymers and dyes
    - The common painkillers aspirin, paracetamol, ibuprofen and morphine all contain benzene rings

Examples of aromatic compounds including benzene table

Functional Group	Example	Name
Arene		propylbenzene
Chlorobenzene		2-methylchlorobenzene
Phenol		2,3-dimethyl phenol

Structure of Benzene

- The structure of benzene was determined many years ago, by the German chemist Friedrich August Kekulé
- The structure consists of 6 carbon atoms in a hexagonal ring, with alternating single and double carbon-carbon bonds
    - This suggests that benzene should react in the same way as an unsaturated alkene
    - However, this is not the case

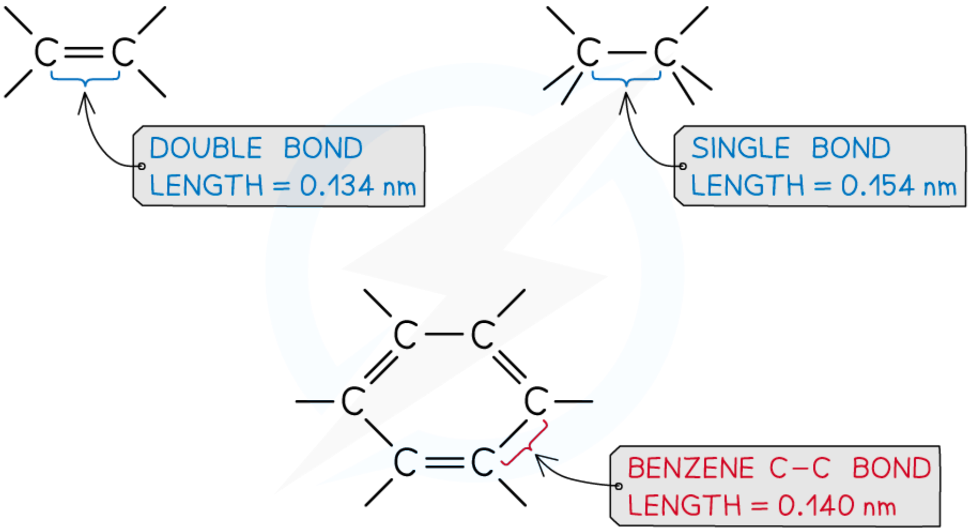


Like other aromatic compounds, benzene has a planar structure due to the sp^2 hybridisation of carbon atoms and the conjugated π system in the ring

- Each carbon atom in the ring forms three σ bonds using the sp^2 orbitals
- The remaining p orbitals overlap laterally with p orbitals of neighbouring carbon atoms to form a π system
- This extensive sideways overlap of p orbitals results in the electrons being delocalised and able to freely spread over the entire ring causing a π system
  - The π system is made up of two ring shaped clouds of electron density - one above the plane and one below it

- Benzene and other aromatic compounds are regular and planar compounds with bond angles of 120 °
- The delocalisation of electrons, as shown below, means that all of the carbon-carbon bonds in these compounds are identical and have both single and double bond character
  - Single covalent bonds have a bond order of 1 and double covalent bonds have a bond order of 2
  - The covalent bonds within benzene have a bond order of 1.5

- The bonds all being the same length is evidence for the delocalised ring structure of benzene



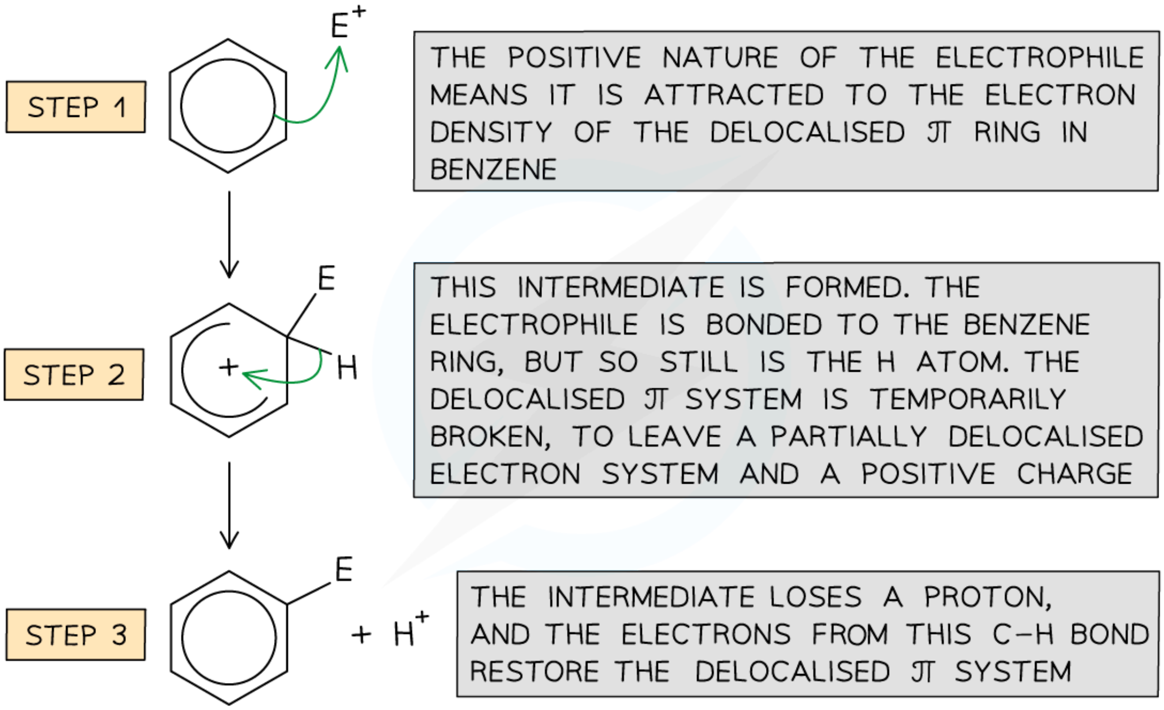
The Delocalisation of Benzene Model

Electrophilic Substitution Mechanism

Reactions of Benzene

- The main reactions which benzene will undergo involve the replacement of one of the hydrogen atoms from the benzene ring
  - This is different to the reactions of unsaturated alkenes, which involve the double bond breaking and the electrophile atoms 'adding on' to the carbon atoms
- These reactions where benzene hydrogen atoms are replaced, are called **electrophilic substitution** reactions
  - The delocalised π system is extremely stable and is a region of high electron density
  - The hydrogen atom is substituted by an electrophile, which is either a positive ion or the positive end of a polar molecule

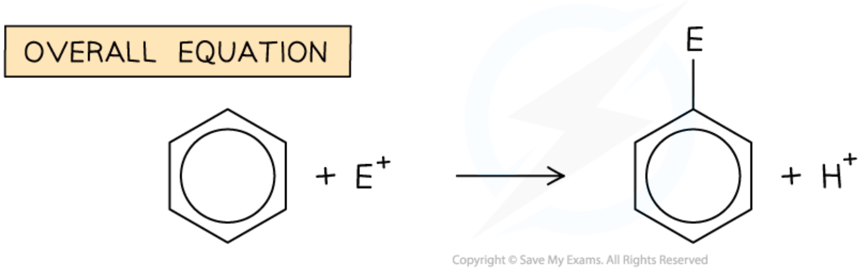
General Electrophilic Substitution Mechanism:



THE POSITIVE NATURE OF THE ELECTROPHILE MEANS IT IS ATTRACTED TO THE ELECTRON DENSITY OF THE DELOCALISED π RING IN BENZENE

THIS INTERMEDIATE IS FORMED. THE ELECTROPHILE IS BONDED TO THE BENZENE RING, BUT SO STILL IS THE H ATOM. THE DELOCALISED π SYSTEM IS TEMPORARILY BROKEN, TO LEAVE A PARTIALLY DELOCALISED ELECTRON SYSTEM AND A POSITIVE CHARGE

THE INTERMEDIATE LOSES A PROTON, AND THE ELECTRONS FROM THIS C–H BOND RESTORE THE DELOCALISED π SYSTEM



Examiner Tip

Make sure you understand the general steps of the electrophilic substitution mechanism and that you can explain what is happening - the same steps happen every time, the only difference is the electrophile used in the reaction!

- There are numerous electrophiles which can react with benzene
    - However, they usually cannot simply be added to the reaction mixture to then react with benzene
    - The electrophile has to be produced in situ, by adding appropriate reagents to the reaction mixture

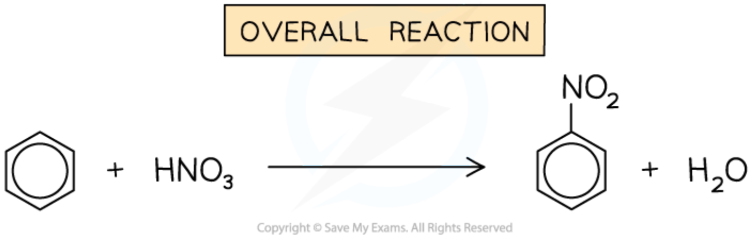
Nitration of Benzene

- You must be able to provide the mechanism for the nitration of benzene via electrophilic substitution
- The electrophilic substitution reaction in arenes consists of three steps:

    1. Generation of an electrophile
    2. Electrophilic attack
    3. Regenerating aromaticity

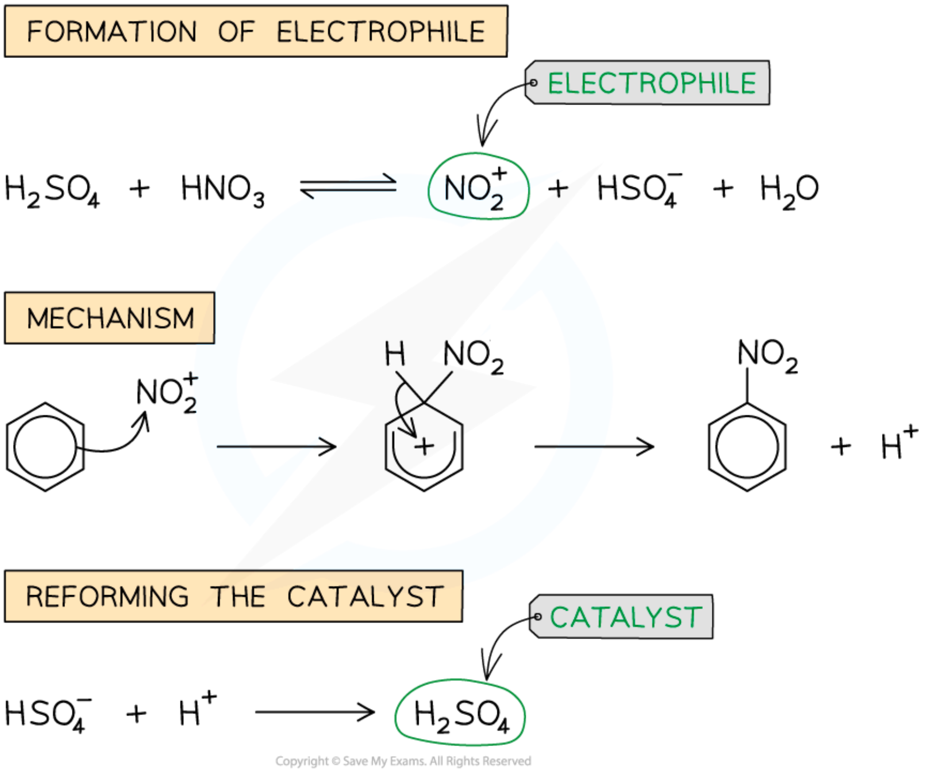
Nitration of Benzene Mechanism

- The nitration of benzene is an example of electrophilic substitution as a hydrogen atom is replaced by a nitro (-NO_2) group



The overall reaction of nitration of arenes

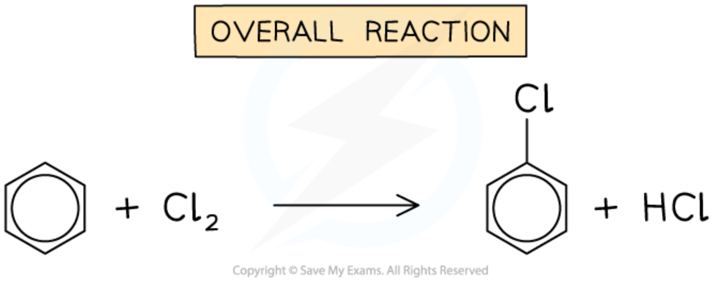
- Step 1: Generation of an electrophile
  - The electrophilic nitronium ion, NO_2^+, is generated by reacting **concentrated** nitric acid, HNO_3, and **concentrated** sulfuric acid, H_2SO_4
  - The sulfuric acid is a catalyst
- Step 2: Electrophilic attack
  - Once the electrophile has been generated, it will carry out an electrophilic attack on the benzene ring
  - The nitrating mixture of HNO_3 and H_2SO_4 is **refluxed** with the arene at 25 - 60 °C
- Step 3: Regenerating aromaticity
  - The aromaticity is restored by the heterolytic cleavage of the C-H bond
- For the nitration of benzene, there is an extra step involving the regeneration of the sulfuric acid catalyst



The different stages in the nitration of benzene

Chlorination of Benzene Mechanism

- The chlorination, or halogenation, of benzene is another example of electrophilic substitution



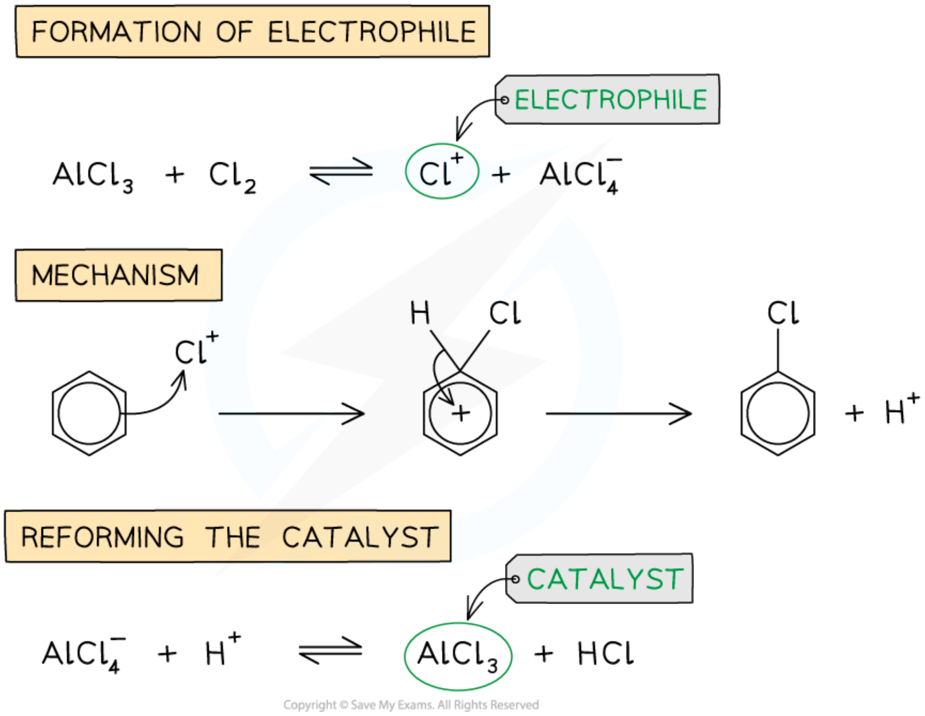
The overall reaction of chlorination of arenes

- Step 1: Generation of an electrophile
  - The electrophilic chlorine cation, Cl^+, is generated by reacting chlorine with anhydrous aluminium chloride, $AlCl_3$
    - The aluminium chloride is electron deficient and acts as a Lewis acid by accepting a lone pair from one of the chlorine atoms
    - As the aluminium forms a dative covalent bond with one of the chlorine atoms, the other chlorine atom becomes a chlorine cation, Cl^+

- Step 2: Electrophilic attack
  - Once the electrophile has been generated, it will carry out an electrophilic attack on the benzene ring

- Step 3: Regenerating aromaticity
  - The aromaticity is, once again, restored by the **heterolytic cleavage** of the C-H bond

- For the chlorination of benzene, there is an extra step involving the regeneration of the aluminium chloride catalyst



The different stages in the chlorination of benzene

20.1.4 Reduction Reactions

Reduction Reactions

Carbonyl compounds

- Alcohols can be oxidised to carbonyl compounds in the presence of a suitable oxidising agent
  - Primary alcohol → aldehyde → carboxylic acid
  - Secondary alcohol → ketone
  - Tertiary alcohol - no reaction

- These reactions can be reversed in the presence of a suitable reducing agent
  - Carboxylic acid → aldehyde → primary alcohol
  - Ketone → secondary alcohol

- The two most common reducing agents for carbonyl compounds are:

  1. Lithium aluminium hydride, $LiAlH_4$, in anhydrous conditions, commonly dry ether, followed by the addition of aqueous acid
     - This is the stronger of these reducing agents and can reduce carboxylic acids

  2. Sodium borohydride, $NaBH_4$, in aqueous or alcoholic solutions
     - This is the less hazardous of these reducing agents but it cannot reduce carboxylic acids

- Both of these reagents produce the nucleophilic hydride ion, H^-

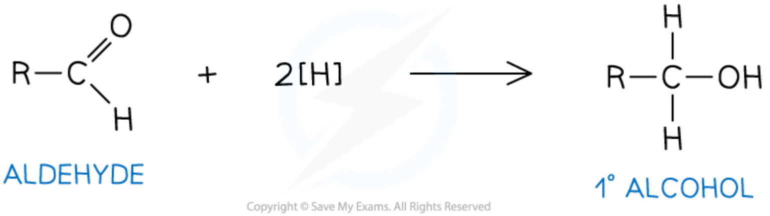
Examiner Tip

You can be expected to know typical conditions and reagents of all reactions, e.g. catalysts, reducing agents, reflux, etc.However, you do not need to know more precise details such as specific temperatures

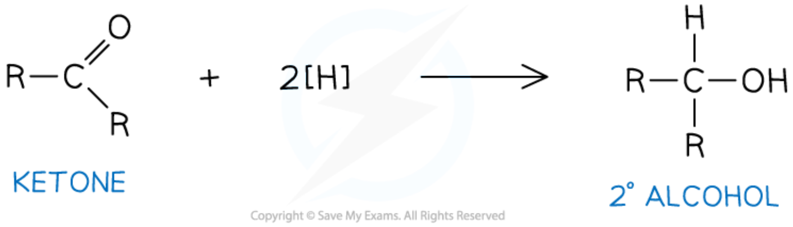
Reduction Reactions

- Equations for reduction reactions can be written using [H] to represent the reducing agent
- Carboxylic acid to a primary alcohol (using $LiAlH_4$ refluxed in dry ether, followed by dilute acid)
  - Remember that $NaBH_4$ cannot reduce carboxylic acids

- Aldehyde to a primary alcohol (using $LiAlH_4$ or $NaBH_4$)



- Ketone to a secondary alcohol (using $LiAlH_4$ or $NaBH_4$)

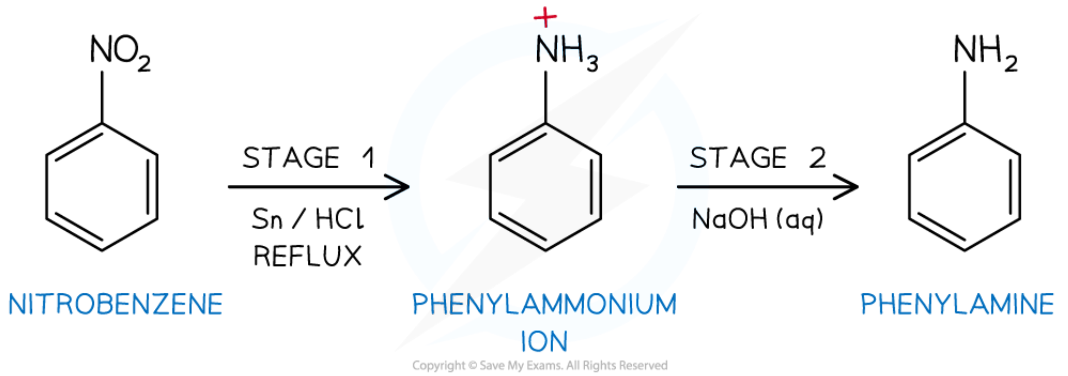


Examiner Tip

Take care if you are asked about the formation of an aldehyde from a carboxylic acidYou have to use $LiAlH_4$ refluxed in dry ether, followed by dilute acid but this reaction cannot be stopped at the aldehyde because the $LiAlH_4$ is too powerfulTo form an aldehyde from a carboxylic acid, you have to reduce the carboxylic acid down to a primary alcohol and then oxidise it back up to the aldehyde

Reduction of nitrobenzene

- Nitrobenzene, $C_6H_5NO_2$, can be reduced to phenylamine, $C_6H_5NH_2$, according to the following two-stage reaction:



The two-stage reduction reaction of nitrobenzene to phenylamine

Stage 1 – Reduction of nitrobenzene

- $C_6H_5NO_2\ (l) + 3Sn\ (s) + 7H^+\ (aq) \rightarrow C_6H_5NH_3^+\ (aq) + 3Sn^{2+}\ (aq) + 2H_2O\ (l)$
- Nitrobenzene, $C_6H_5NO_2$, is reacted with tin, Sn, and concentrated hydrochloric acid, HCl
- The reaction mixture is heated under reflux in a boiling water bath
- The phenylammonium ions, $C_6H_5NH_3^+$, are protonated due to the acidic conditions

Stage 2 – Formation of phenylamine

- $C_6H_5NH_3^+\ (aq) + OH^-\ (aq) \rightarrow C_6H_5NH_2\ (l) + H_2O\ (l)$
- The phenylammonium ions, $C_6H_5NH_3^+$, are deprotonated by the addition of sodium hydroxide solution, NaOH (aq)