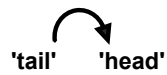
Understanding Curly Arrows

The purpose of the curly arrow is to show movement of electrons from one site to another. Electrons move from the 'tail' to the 'head'. Curly arrows depict the flow of electrons.



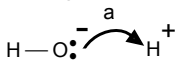
source (electron donor) destination (electron acceptor)

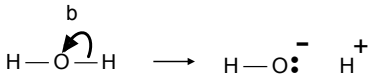
There are 3 classes of reaction arrows.

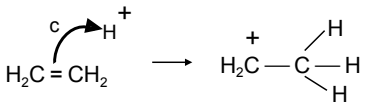
lone pair → bond pair
bond pair → lone pair
bond pair → bond pair

When a pair of electrons are being donated from the **'tail'**, the atom at this site will have a formal 'loss' of 1 electron, making its charge more positive by 1.

When a pair of electrons are being accepted at the **'head'**, the atom at this site will have a formal 'gain' of 1 electron, making its charge more negative by 1.

1. lone pair → bond pair  Arrow a: lone pair → bond pair

2. bond pair → lone pair  Arrow b: bond pair → lone pair

3. bond pair → bond pair  Arrow c: bond pair → bond pair

Alkanes Undergo Free Radical Substitution

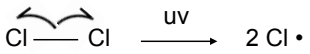
Organic Compound: alkanes
Reagents: Cl_2 (g) or Br_2 (l)
Conditions: uv or heat

A **free radical** is an atom or group of atoms with an **unpaired electron**, formed from the homolytic cleavage of a single covalent bond. It is very reactive.
Note: The reaction **will not proceed in the dark** at room temp.

When methane reacts with chlorine in sunlight, the yellowish green colour of chlorine fades and white fumes of hydrochloric gas can be observed.

$$CH_4\,(g) + Cl_2\,(g) \xrightarrow{uv} CH_3Cl\,(g) + HCl\,(g)$$

Initiation: Formation of free radicals via homolytic fission of the Cl–Cl bond:



Propagation: Re-generation of halide radicals via chain reaction:

$Cl\bullet + CH_4 \longrightarrow \bullet CH_3 + HCl$ -------- (a)
$\bullet CH_3 + Cl_2 \longrightarrow CH_3Cl + Cl\bullet$ -------- (b)

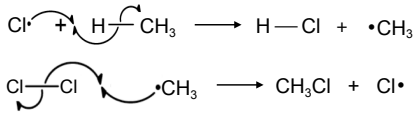
Note: The sum of the two propagation steps is the overall reaction.

Then (a),(b),(a),(b)… if Cl_2 is in excess, and a mixture of products will be formed.

Termination: Collision of two free radicals to form a single covalent bond.

$Cl\bullet + Cl\bullet \longrightarrow Cl_2$
$Cl\bullet + \bullet CH_3 \longrightarrow CH_3Cl$
$\bullet CH_3 + \bullet CH_3 \longrightarrow CH_3CH_3$

If curly arrows are needed to be shown in the mechanism



Electrophilic Addition

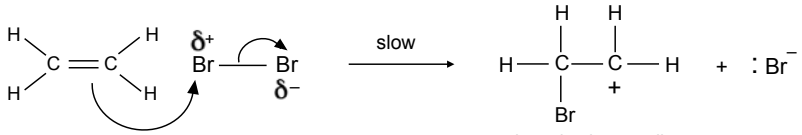
Organic Compound:	alkenes
Reagents:	Br_2 (l) in CCl_4
Conditions:	room temperature, dark

When ethene reacts with bromine, the reddish brown colour of bromine decolourises.

$CH_2{=}CH_2 + Br_2 \longrightarrow CH_2BrCH_2Br$

Step 1:

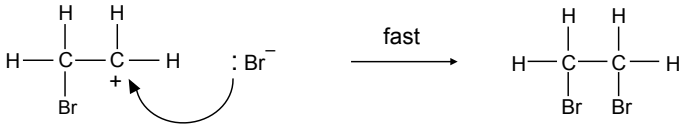
- carbon-carbon double bond is highly electron-rich.
- π electron cloud of ethene polarises the Br—Br bond, i.e. the bromine molecule becomes $^{\delta+}Br—Br^{\delta-}$.
- $^{\delta+}Br$ atom of the bromine molecule acts as an **electrophile** and is strongly attracted to the electron rich C=C bond to form a bromide ion and a positively charged carbocation intermediate.



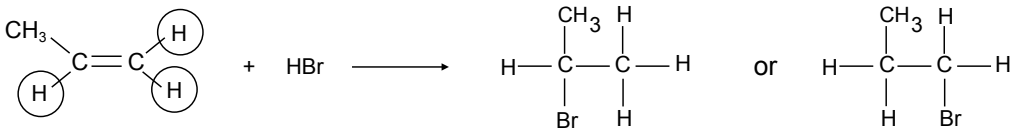
carbocation intermediate

Step 2:

- Carbocation intermediate is rapidly attacked by the bromide ion to form the product 1,2-dibromoethane.



Electrophilic Addition: addition of HX to an unsymmetrical alkene



2-bromopropane (major product)

1-bromopropane (minor product)

Markovnikov's Rule

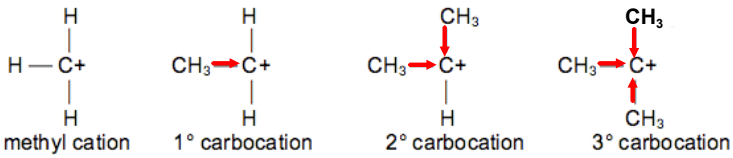
When HX (X: Cl, Br or I) adds to a C=C bond in an unsymmetrical alkene, the major product is the one in which the hydrogen atom attaches itself to the carbon atom already carrying the **larger number of hydrogen atoms**.

The reason why 2-bromopropane is the major product lies in the chracteristics of the 2 carbocations. Carbocations can be classified as 1°, 2° and 3° based on number of alkyl groups attached to the carbon atom carrying the positive charge. A more stable carbocation is formed faster than a less stable carbocation.

Alkyl groups are electron-donating which disperse the positive charge on the carbocation, stabilising the carbocation. Hence, the greater the number of alkyl groups attached to carbocation, the more stable the carbocation.

Stability of carbocation

3 °> 2° > 1° > methyl cation



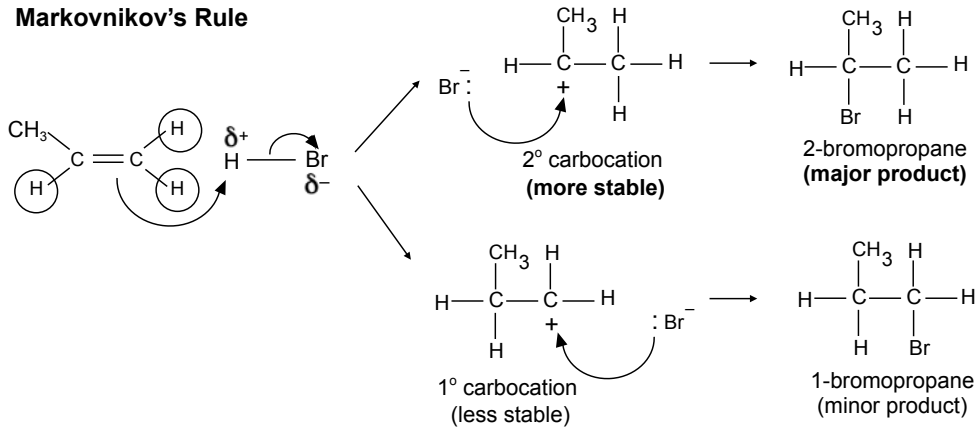
methyl cation | 1° carbocation | 2° carbocation | 3° carbocation

How does electron-donating groups stabilise a carbocation?

For the carbocation, when the positive charge on the carbon bearing it is made less intense and 'concentrated', there is a lesser tendency for it to be attacked by nucleophiles, making it more stable. To **DISPERSE** the positive charge is to spread the charge over the entire ion rather than having it residing on the single carbon atom.

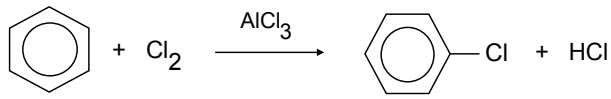
Thus more electron-donating alkyl groups attached to the carbocation will result in greater charge dispersal and a more stable carbocation.

Markovnikov's Rule



Electrophilic Substitution

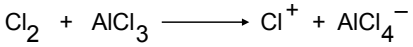
Organic Compound:	arenes
Reagents:	Cl_2 with a lewis catalyst e.g. anhydrous $AlCl_3$ or anhydrous $FeCl_3$ or Fe
Conditions:	room temperature



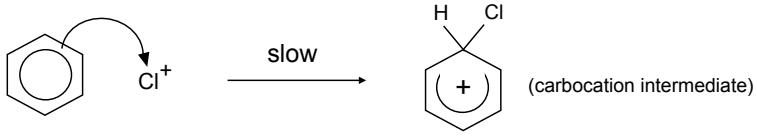
If Fe is used instead, $FeCl_3$ can be generated in situ.

$3Cl_2 + 2Fe \rightarrow 2FeCl_3$

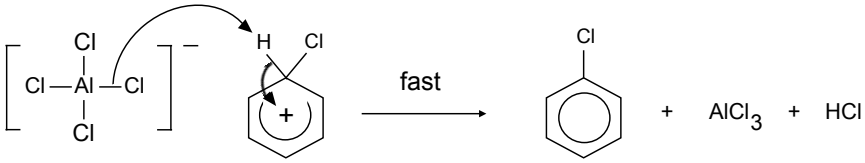
Step 1: Generation of electrophile, Cl^+



Step 2: Electron-rich benzene attacks the electrophile to form an intermediate.

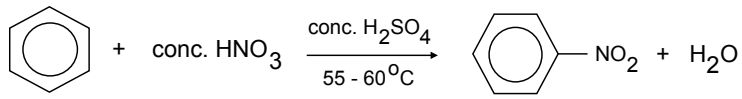


Step 3: Stability of aromatic ring regenerated with loss of proton.



Electrophilic Substitution

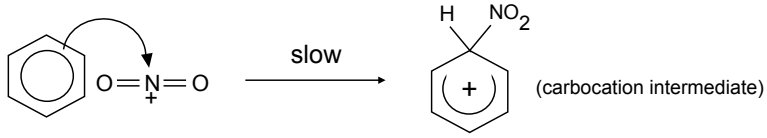
Organic Compound: arenes
Reagents: conc. HNO_3, conc. H_2SO_4
Conditions: 55 - 60^oC



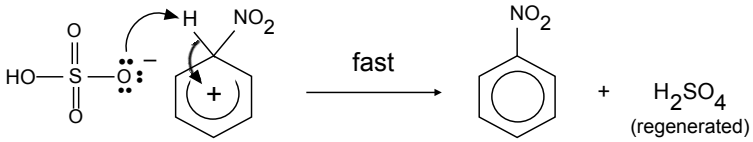
Step 1: Generation of electrophile, NO_2^+

$$HNO_3 + 2H_2SO_4 \longrightarrow NO_2^+ + H_3O^+ + 2HSO_4^-$$

Step 2: Electron-rich benzene attacks the electrophile to form an intermediate.



Step 3: Stability of aromatic ring regenerated with loss of proton.



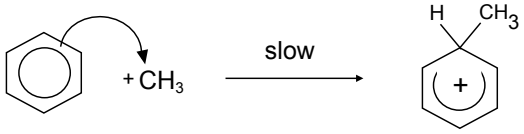
Electrophilic Substitution (Friedel-Crafts *alkylation)*

Organic Compound: arenes
Reagents: CH_3Cl with a lewis acid catalyst e.g. anhydrous $AlCl_3$ or anhydrous $FeCl_3$
Conditions: room temperature

Step 1: Generation of electrophile, CH_3^+

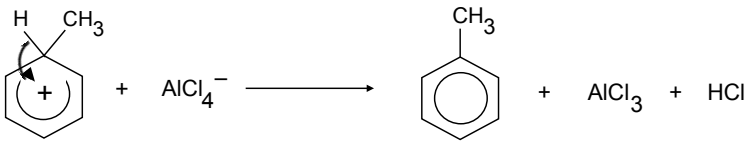
$$CH_3Cl + AlCl_3 \longrightarrow \overset{+}{C}H_3 + AlCl_4^-$$

Step 2: Electrophilic attack on benzene by electrophile CH_3^+



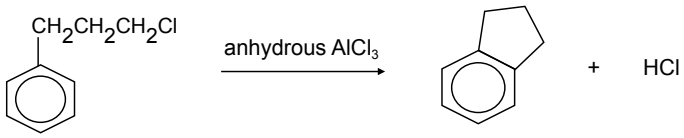
carbocation intermediate

Step 3: Loss of proton

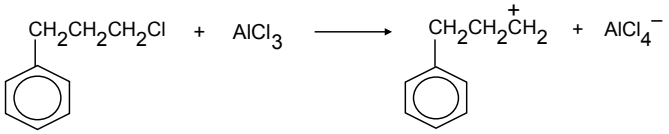


Electrophilic Substitution (Friedel-Crafts ***alkylation*** to form a cyclic compound)

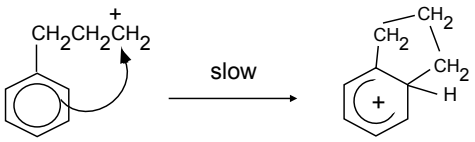
Draw the mechanism for the following.



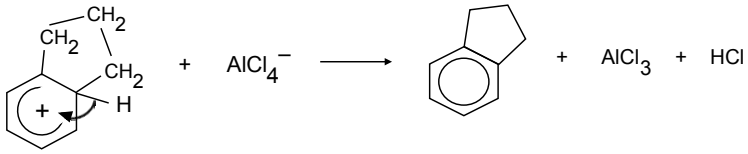
Step 1: Generation of electrophile, $C_6H_5CH_2CH_2CH_2^+$



Step 2: Electrophilic attack on benzene by electrophile, $C_6H_5CH_2CH_2CH_2^+$



Step 3: Loss of proton

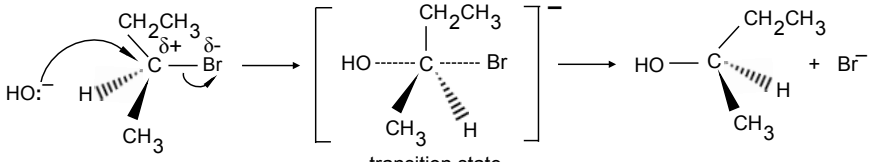


Nucleophilic Substitution (S_N2 mechanism)

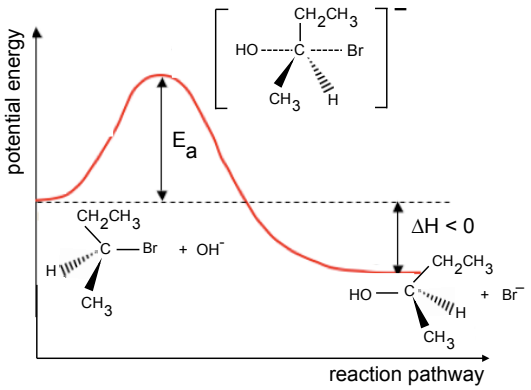
Organic compound : alkyhalides
Reagent and condition : **NaOH (aq), heat under reflux**

$CH_3CHBrCH_2CH_3 + NaOH \xrightarrow{\text{heat under reflux}} CH_3CH(OH)CH_2CH_3 + NaBr$

S_N2 mechanism

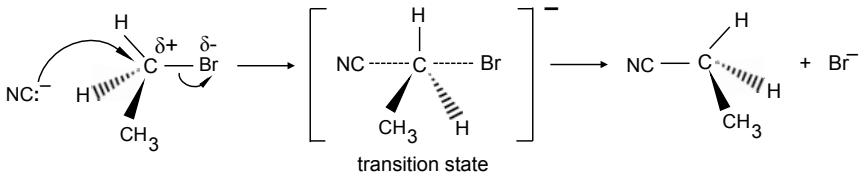


- **S_N2 - One step mechanism**
- The nucleophile, OH^- attacks the δ+ carbon from the **opposite side** to the halogen atom.
- The new carbon-nucleophile bond is forming while the old carbon-halogen bond is breaking **simultaneously** to form the pentavalent transition state or activated complex which cannot be isolated.
- The reaction follows a **2nd order kinetics** and the rate law is said to be **bimolecular**. rate = k[RX][OH^-]
- The chiral centre is **inverted** as compared to the reactant.
- Relative rate of reaction: 3° < 2° < 1° < CH_3X (fastest)
  ⇒ **S_N2 is preferred for 1° halogenoalkane**



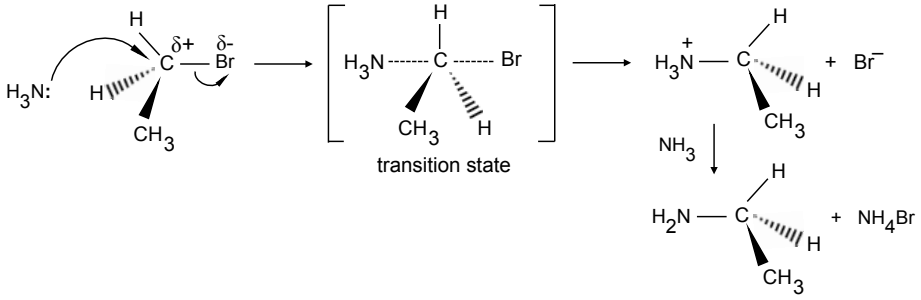
Nucleophilic Substitution (S_N2 mechanism)

Organic compound : alkylhalides
Reagent and condition : **ethanolic KCN, heat under reflux**



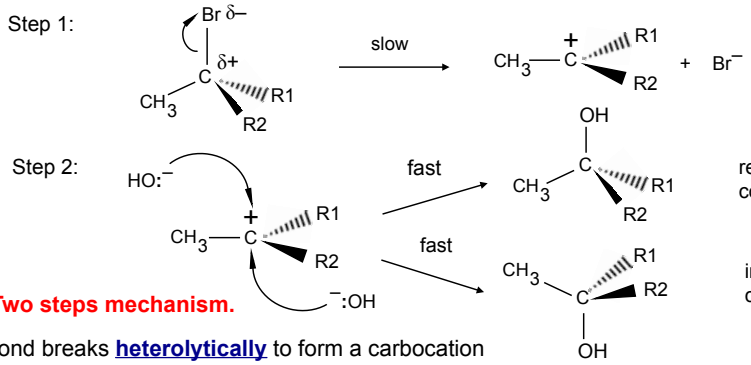
Note: It is the lone pair on the carbon of CN^- (not N) that attacks the electron deficient carbon of the alkylhalide. This is because the **negative charge is on the carbon** atom. This makes the carbon atom more **electron rich** and **more nucleophilic** than the nitrogen atom.

Organic compound : alkylhalides
Reagent and condition : **excess conc. NH_3 in ethanol, heat in sealed tube**

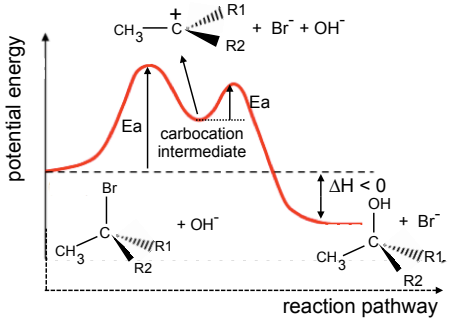


Nucleophilic Substitution (S_N1 mechanism)

Organic compound : alkyhalides
Reagent and condition : NaOH (aq) , heat under reflux



- **S_N1 - Two steps mechanism.**
- C-Br bond breaks **heterolytically** to form a carbocation intermediate. This is the rate determining step.
- Carbocation is trigonal planar, the nucleophile may attack the carbocation from ***either face with equal probability***.
- If reaction is carried on a chiral halogenoalkane, a **racemic mixture** (optically inactive) is formed.
- The reaction follows **1st order kinetics** and the rate law is said to be **unimolecular**. rate = k[RBr]
- Relative rate of reaction: $CH_3X < 1^o < 2^o < 3^o$ (fastest)
  ⇒ **S_N1 is preferred for 3° halogenoalkane**



Factors that affect the rate of S_N1 and S_N2 mechanism

1. **C-X bond strength**

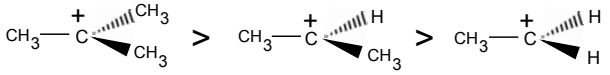
   The order of reactivity of CH_3X to S_N1 and S_N2 mechanism:

   $CH_3Cl < CH_3Br < CH_3I$ (fastest) (Note: CH_3F is unreactive due to the strong C-F bond)

   Decreasing C-X bond strength

2. **S_N1 mechanism is favoured by <u>factors that stabilise the carbocation</u>:**

   Stability of carbocation:

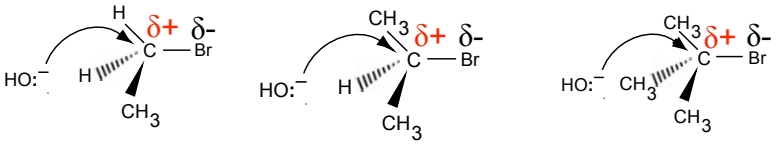
   

   3° carbocation > 2° carbocation > 1° carbocation

   Electron donating alkyl groups **<u>disperse</u>** the positive charge of the carbocation. Since the positive charge of the 3° carbocation is dispersed to the greatest extent, it is most **<u>stable</u>** compared to 2° and 1° carbocation ⇒ **<u>S_N1 is preferred for 3° halogenoalkane</u>.**

2. **S_N2 mechanism is favoured by <u>less steric hindrance</u>.**

   The presence of alkyl groups **<u>blocks</u>** the backside approach of the nucleophile.
   ⇒ **S_N2 is preferred for 1° halogenoalkane** due to **<u>less steric hindrance</u>**.

   1° alkylhalide 2° alkylhalide 3° alkylhalide

Nucleophilic Addition

Organic Compound:	carbonyl compounds
Reagents:	HCN with trace KCN or NaOH
Conditions:	cold

Step 1: Generation of the nucleophile, CN^- (use of trace NaOH)

$HCN \rightleftharpoons H^+ + CN^-$ or $HCN + OH^- \longrightarrow CN^- + H_2O$

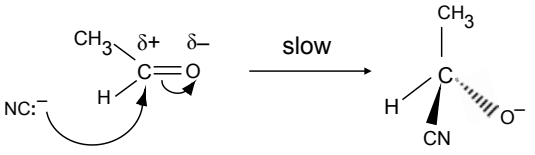
Or Generation of the nucleophile, CN^- (use of trace KCN)

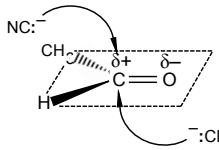
$KCN\ (aq) \rightarrow K^+\ (aq) + CN^-\ (aq)$

Why is NaOH or KCN added?

Since rate = k[RCHO][CN^-] and HCN is a very weak acid, the addition of NaOH or KCN is needed to increase the concentration of CN^- to increase the rate of reaction.

Step 2: Nucleophilic attack by the CN^- ion on the electron-deficient carbonyl carbon to form a tetrahedral intermediate anion.





The molecule is trigonal planar about the carbonyl carbon. The nucleophile may attack the carbonyl carbon equally from the top or bottom, hence resulting in a **<u>racemic mixture</u>**.

Step 3: Protonation of the anionic intermediate, regenerating the CN^- anion.