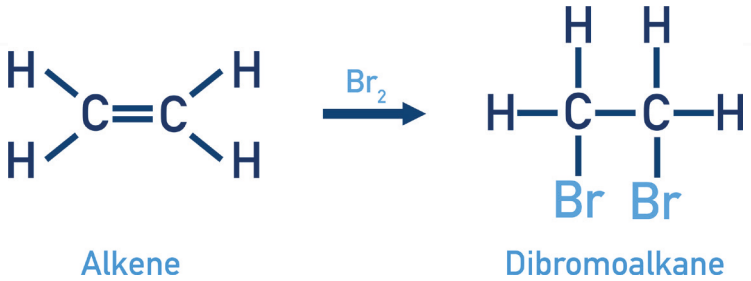
Reaction

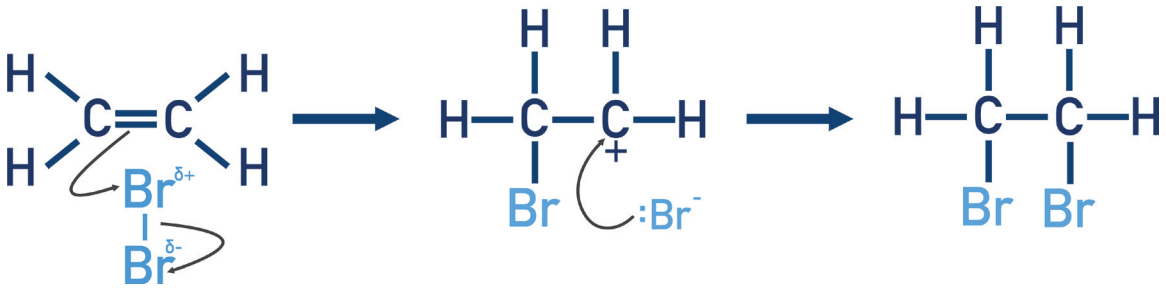
REACTANTS: Alkene and Bromine (Br_2)
CONDITIONS: Non-polar organic solvent (or pure liquid bromine)
PRODUCT: Dibromoalkane
REACTION TYPE: Electrophilic Addition

REACTION: (example of ethene)



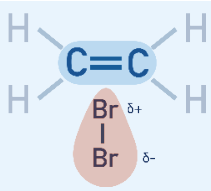
Mechanism

Br_2 acts as an electrophile so the bromine-bromine bond is polarised by the carbon-carbon double bond so the bromine atom with a partial positive charge accepts an electron pair from the carbon-carbon double bond. During the reaction the carbon-carbon double bond breaks, forming a postively charged carbon (carbocation). The negatively charged bromide ion bonds with the carbocation. Br_2 is 'added' across the double carbon-carbon bond. ***Addition reaction.***



Notes:

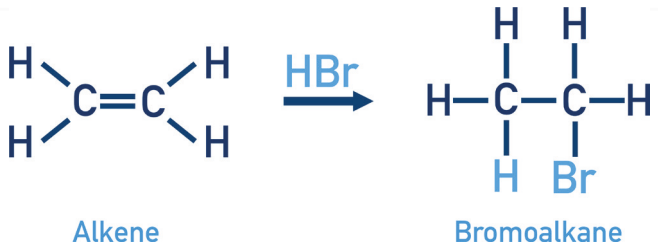
- The high electron density in the carbon-carbon double bond (pi-bond) polarises the bromine molecule to create the $Br^{\delta+}$ electrophile.
- *This reaction is often used to identify an alkene as the colour of bromine water changes from orange / brown to colourless when mixed with an alkene (due to the above reaction).*



Reaction

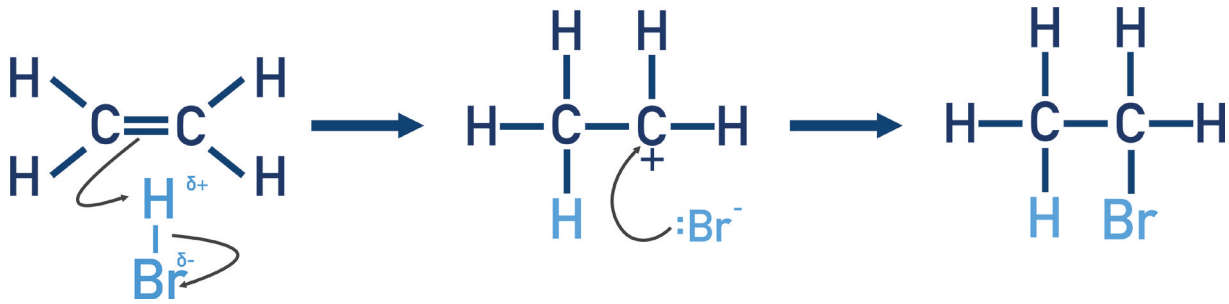
REACTANTS: Alkene and HBr (Hydrogen Bromide)
PRODUCT(S): Bromoalkane
REACTION TYPE: Electrophilic Addition

REACTION: (example of ethene)



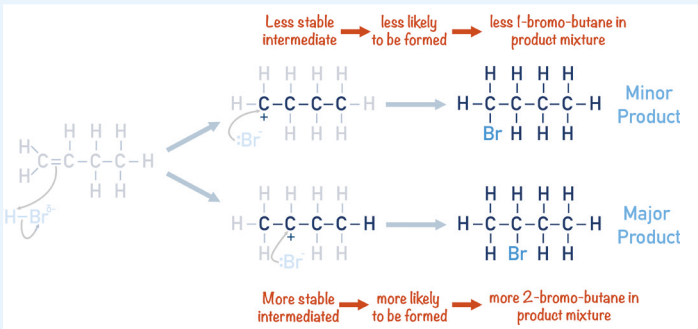
Mechanism

HBr acts as an electrophile because its hydrogen atom (with a partial positive charge) accepts an electron pair from the carbon-carbon double bond. During the reaction the carbon-carbon double bond breaks, forming a postively charged carbon ion (carbocation). The negatively charged bromide ion bonds with the carbocation. HBr is 'added' across the carbon-carbon double bond. ***Addition reaction.***



Notes:

- If a primary or secondary carbocation can be formed during the reaction, **the secondary carbocation will form more readily than the primary carbocation** - creating 'major' and 'minor' products*.
- The secondary carbocation is more stable due to increased positive inductive effect from neighbouring alkyl chains.
- **The product mixture will contain more of the major product than the minor product.*



Reaction

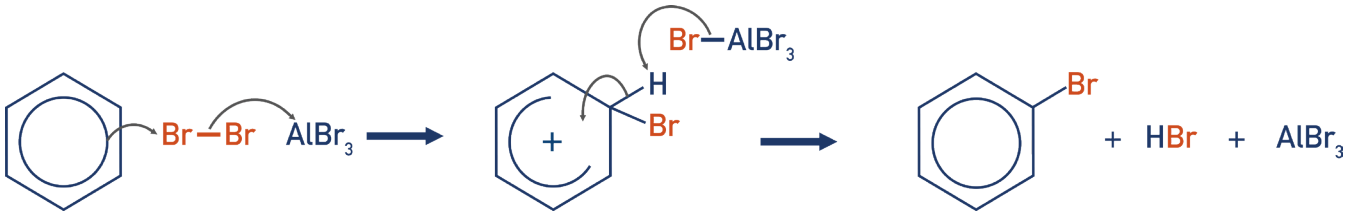
REACTANTS: Benzene and Halogen
CONDITIONS: Halogen carrier ($AlCl_3$, $AlBr_3$ or Fe)
PRODUCT: Halogenated Arene (chloro-benzene, bromo-benzene)
REACTION TYPE: Electrophilic Substitution, *Halogenation*

REACTION: (example of benzene)

Benzene Bromobenzene

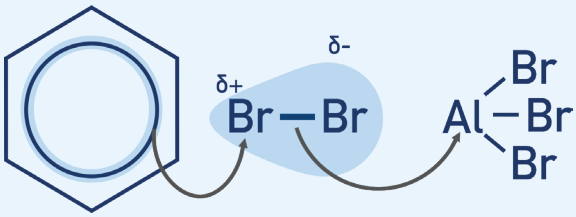
Mechanism

Bromine molecule **acts as an electrophile because it is polarised sufficiently by a halogen carrier ($AlBr_3$)** and accepts an electron pair from the delocalised ring of electrons in the benzene ring. A carbon-bromine bond forms. The carbon-hydrogen bond breaks to the give electron pair back to delocalised ring of electrons. Br replaces H on benzene ring. ***Substitution reaction***.



Notes:

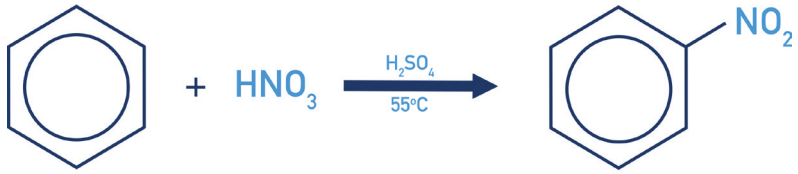
- Benzene is unable to undergo halogenation without a halogen carrier as the delocalised electron ring is unable to polarise the halogen moleucle enough to form an electrophile.
- The halogen carrier poalrises the halogen molecule to the point of enabling one of the halogen atoms (now with a partial positive charge) to act as an electrophile and accept a pair of electrons from benzene.



Reaction

REACTANTS: Benzene and Nitric Acid
CONDITIONS: 55°C and conc. sulfuric acid (H_2SO_4)
PRODUCT: Nitrobenzene
REACTION TYPE: Electrophilic Substitution, *Nitration*

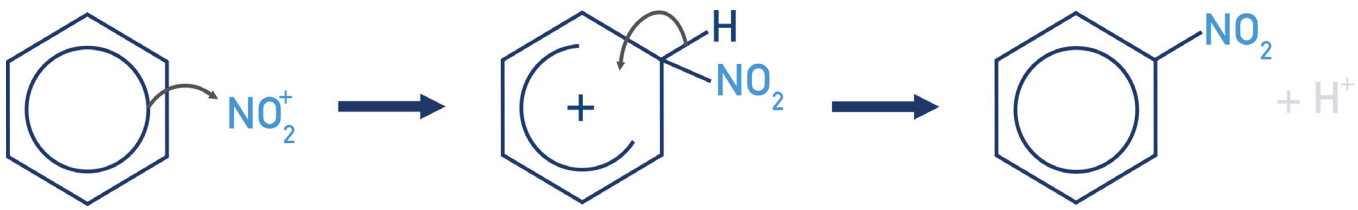
REACTION: (example of benzene)



Benzene Nitrobenzene

Mechanism

Nitronium (NO_2^+) ion **acts as an electrophile due to its positively charged nitrogen atom accepting an electron pair** from the delocalised ring of electrons in the benzene ring. A Carbon-nitrogen bond forms. The carbon-hydrogen bond breaks to give electron pair back to delocalised ring of electrons. NO_2^+ ion replaces H on benzene ring - ***substitution reaction***.



Notes:

- Nitronium ion is formed by the reaction of concentrated nitric acid with concentrated sulfuric acid

$$HNO_3 + H_2SO_4 \longrightarrow H_2NO_3^+ + HSO_4^-$$

$$H_2NO_3^+ \longrightarrow NO_2^+ + H_2O$$

Nitronium Ion

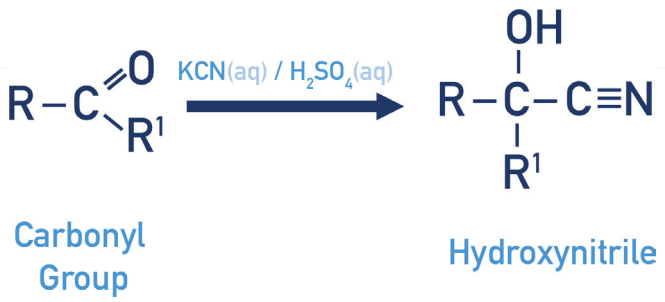
- H^+ ion removed from benzene ring combines with hydrogen sulfate (HSO_4^-) ion to reform catalyst H_2SO_4:

$$H^+ + HSO_4^- \rightarrow H_2SO_4$$

Reaction

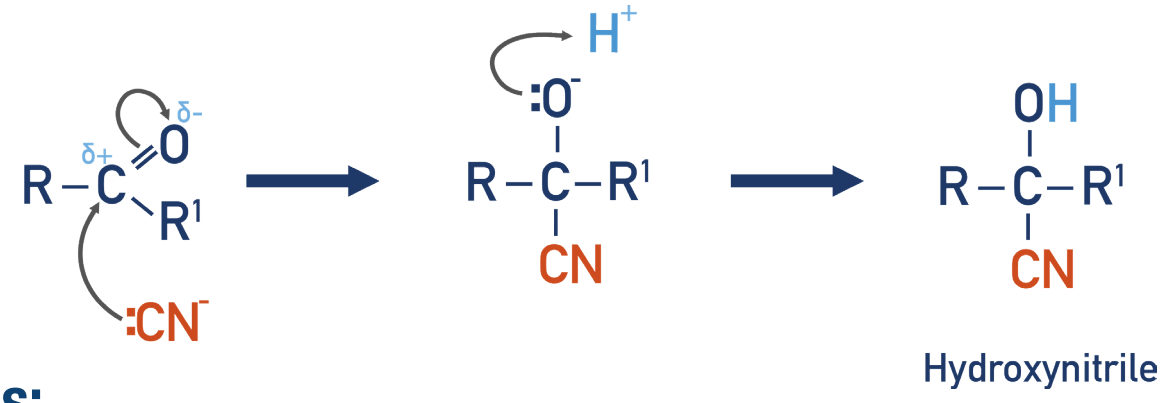
REACTANTS: Carbonyl (aldehyde or ketone) and KCN (in acid)
PRODUCT: Hydroxynitrile
REACTION TYPE: Nucleophilic Addition

REACTION:



Mechanism

Cyanide ion (:CN^-) comes from KCN(aq) and **acts as a nucleophile due to its lone pair of electrons, attacking the carbon (with partial positive charge) in the carbonyl group**. Carbon-carbon bond forms. The carbon-oxygen double bond breaks to a single bond, giving the oxygen a negative charge. The negative oxygen is protonated in dilute acid (H_2SO_4), forming a hydroxyl group. Hydroxynitrile is formed. CN and H are added to the carbonyl. ***Addition reaction.***



Notes:

- HCN is sometimes written as the reactant, but HCN is very reactive and dangerous however. By using KCN in dilute acid, the same product can be formed as with HCN.

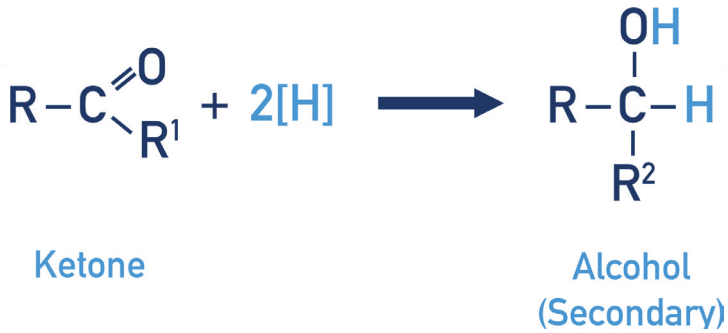
$$HCN + RR'CO \rightarrow RR'C(OH)CN$$

- If a chiral carbon centre is formed in the product, the final product mixture will be **racemic** containing both enantiomers in a 50:50 ratio. This is because carbonyl groups are planar and there is equal chance of the :CN^- nucleophile attacking the carbonyl group from above or below the plane - producing two possible enantiomers in equal amounts.

Reaction

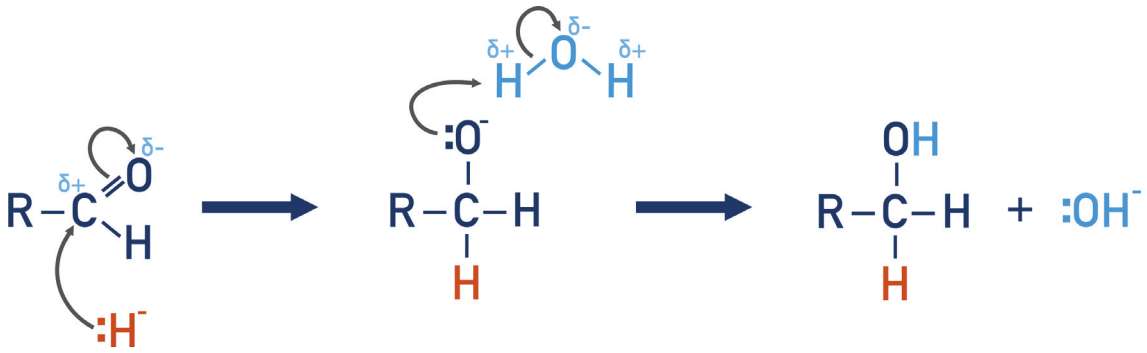
REACTANTS: Carbonyl (aldehyde or ketone) and $NaBH_4$ or $LiAlH_4$
PRODUCT: Alcohol
REACTION TYPE: Nucleophilic Addition, *reduction*

REACTION: (example of ketone)



Mechanism

Hydride ion (:H⁻) comes from reducing agent ($NaBH_4$ or $LiAlH_4$*) and **acts as a nucleophile due to its lone pair of electrons attacking the carbon (with partial positive charge) in the carbonyl group**. A carbon-hydrogen bond forms. The carbon-oxygen double bond breaks to a single bond, giving the oxygen a negative charge. The negative oxygen is protonated by water, forming a hydroxyl group and a hydroxide ion. Alcohol is formed, H is added to the carbonyl.***Addition reaction.***



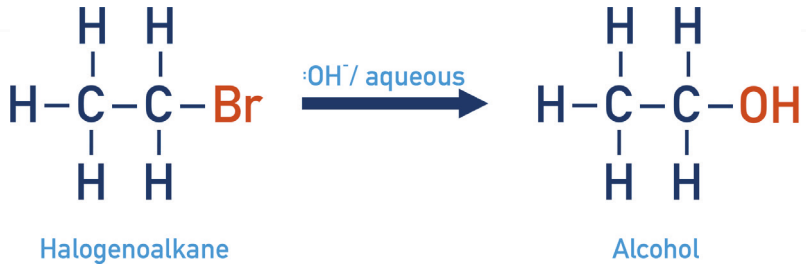
Notes:

- Aldehydes form **primary alcohols** when reduced.
- Ketones form **secondary alcohols** when reduced.
- *$NaBH_4$ and $LiAlH_4$ are reducing agents, they are able to provide hydride (:H⁻) ions that are needed for the reduction of carbonyls.

Reaction

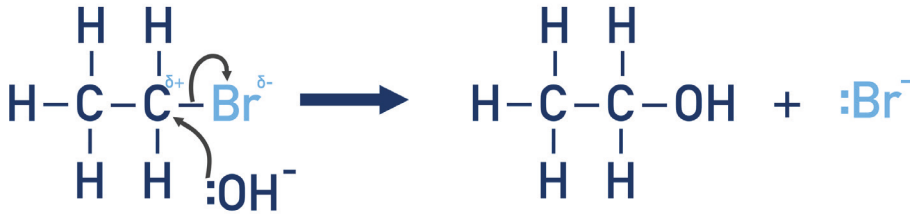
REACTANTS: Halogenoalkane and Sodium Hydroxide, *NaOH* (for OH^- ions)
CONDITIONS: Aqueous ('aq' - water present)
PRODUCT(S): Alcohol and Halide Ion (*sodium halide salt if sodium hydroxide used*)
REACTION TYPE: Nucleophilic Substitution

REACTION: (example of bromoethane)



Mechanism

Hydroxide ion (OH^-) acts as a nucleophile and attacks the partially positive carbon atom in the carbon-halogen bond. The carbon-halogen breaks, forming alcohol and halide ion. OH group is **substituted** for the halogen group.



Notes:

- Reaction **must be carried out in aqueous conditions (in water), otherwise an elimination reaction will occur and an alkene will be formed.**
- The strength of the carbon-halogen bond (bond enthalpy) determines the speed of the reaction. The stronger the bond, the slower the nucleophilic substitution reaction. *C-F bond is strongest, giving the slowest reaction; C-I bond is weakest, giving the fastest reaction.*

Reaction

REACTANTS: Alkane and Halogen
CONDITIONS: U.V (ultraviolet) light
PRODUCT(S): Halogenoalkane and Hydrogen Halide
REACTION TYPE: Free Radical Substitution

REACTION: (example of methane and chlorine)

ultraviolet light required for reaction to occur

$$CH_4 + Cl_2 \xrightarrow{u.v} CH_3Cl + HCl$$

Mechanism

INITIATION STEP: Halogen molecule undergoes heterolytic fission to form radical species:

$$Cl_2 \xrightarrow{u.v} 2Cl\bullet$$

PROPAGATION STEP: Radical species reacts with alkane to form alkyl radical and HCl. Alkyl radical then reacts with halogen molecule, reforming another halogen radical, creating a **chain reaction**:

new radical formed

$$CH_4 + Cl\bullet \longrightarrow \bullet CH_3 + HCl$$

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

(new) radical formed

TERMINATION STEP: Radical species combine to end chain reaction:

Two unpaired electrons combine to form a bond between the two species

$$Cl\bullet + Cl\bullet \longrightarrow Cl_2$$

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

$$\bullet CH_3 + \bullet CH_3 \longrightarrow CH_3CH_3$$

Products are no longer radicals

Notes:

- Heterolytic fission is the even breaking of a covalent bond (each bonded atom gets an electron and becomes a radical species).
- UV light provides the energy required for hetereolytic fission.
- Further substitution reactions can occur, eventually forming tetrachloromethane:
  chloromethane to dichloromethane to trichloromethane to tetrachloromethane