Alkanes Combustion

REACTANTS: Alkane and O_2 (oxygen)
CONDITIONS: Excess of Oxygen (for complete combustion)
PRODUCT(S): Carbon Dioxide and Water
REACTION TYPE: Combustion

REACTION: (example of pentane)

$$C_5H_{12} + 8O_2 \longrightarrow 5CO_2 + 6H_2O$$

Alkane Oxygen Carbon Dioxide Water

NOTES:

- When excess oxygen is present complete combustion occurs so carbon dioxide and water are the only products.
- Incomplete combustion of alkanes occurs when oxygen becomes a limiting reagent, leading to the formation of carbon monoxide (CO) and solid carbon particulates (soot).

Alkanes Free Radical Substitution

REACTANTS: Alkanes and Halogen
CONDITIONS: U.V (ultraviolet) light
PRODUCT: Halogenoalkane
REACTION TYPE: Free Radical Substitution

REACTION: (example of methane)

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

Alkane | Chlorine | Chloroalkane | Hydrogen Halide

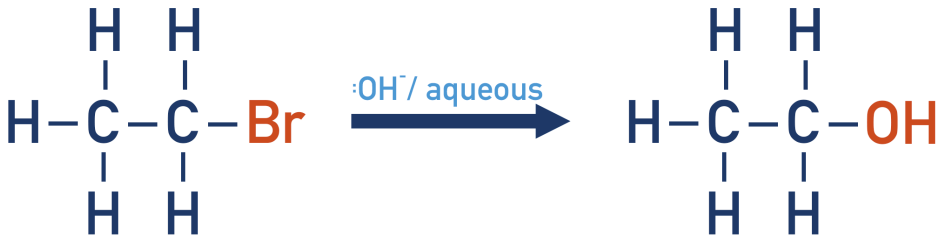
NOTES:

- Chain reaction, occuring in three steps - **initiation**, **propagation** and **termination.** *See mechanism.*
- U.V light is required to homolytically split halogen molecule, forming two radical species.
- Further substitution can occur, forming di, tri and tetra halogenoalkanes.

Halogenoalkanes Substitution (OH^-)

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

REACTION: (example of bromoethane)



Halogenoalkane Alcohol

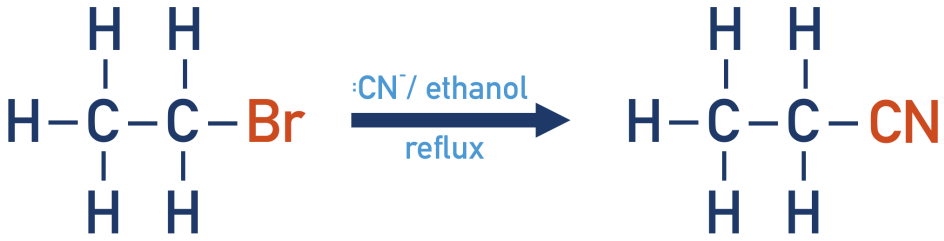
NOTES:

- Rate of reaction is determined by strength of carbon-halogen bond (carbon-flourine bond is strongest giving slowest rate; carbon-iodine bond is weakest, giving fastest rate).
- Rate of hydrolysis can compared using aqueous silver nitrate ($AgNO_3$) within the reaction mixture and timing how long it takes to form precipitate (Cl = **white** ppt, Br = **cream** ppt and I = **yellow** ppt).
- Reaction must be carried out in **aqueous conditions, otherwise an elimination can occur.**

Halogenoalkanes Substitution (CN^-)

REACTANTS: Halogenoalkane and Sodium *or Potassium* Cyanide (NaCN *or KCN*)
CONDITIONS: Heat under reflux, Ethanolic (ethanol as the solvent, **no water present**)
PRODUCT(S): Nitrile and Halide Ion (*forms salt with Na^+ or K^+*)
REACTION TYPE: Nucleophilic Substitution

REACTION: (example of pentane)



Halogenoalkane Nitrile

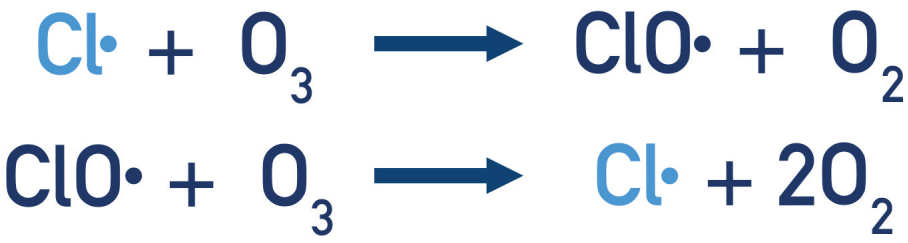
NOTES:

- Rate of reaction is determined by strength of carbon-halogen bond (carbon-flourine bond is strongest, giving slowest rate; carbon-iodine bond is weakest, giving fastest rate).
- Reaction must be carried out in **ethanolic conditions (in ethanol, no water present), otherwise an alcohol is likely to form** rather than the nitrile.
- Reaction is heated under reflux to ensure no volatile substances are lost.

Decomposition (Free Radical) Ozone

REACTANTS: Chlorine Radical and Ozone (O_3)
CONDITIONS: Upper Atmosphere, (u.v light to form chlorine radical)
PRODUCT(S): Oxygen
REACTION TYPE: Decomposition (Free Radical)

REACTION: (example of ozone)



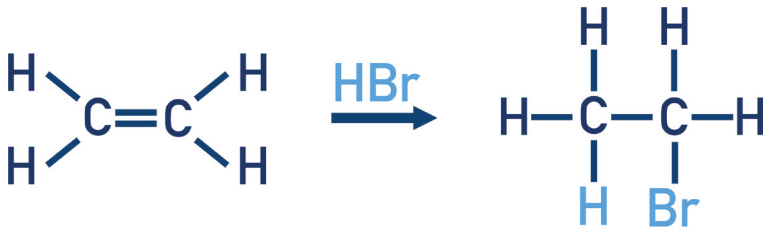
NOTES:

- Chlorine radical is formed by homolytic fission of chlorine molecule in upper atmopshere by u.v light.
- This is a chain reaction as the chlorine radical is reformed and can go on to decompose more ozone molecules.
- Ozone (O_3) prevents u.v radiation from reaching the surface of planet Earth. The use of CFC's (chlorofluourinated carbons) in the 20th century lead to a depletion of ozone in the upper atmosphere; CFCs were banned as a result.

Alkenes Addition (HBr)

REACTANTS: Alkene and Hydrogen Bromide (HBr)
CONDITIONS: Hydrogen Bromide Gas or (concentrated) Hydrobromic Acid
PRODUCT(S): Bromoalkane
REACTION TYPE: Electrophilic Addition

REACTION: (example of ethene)



Alkene Bromoalkane

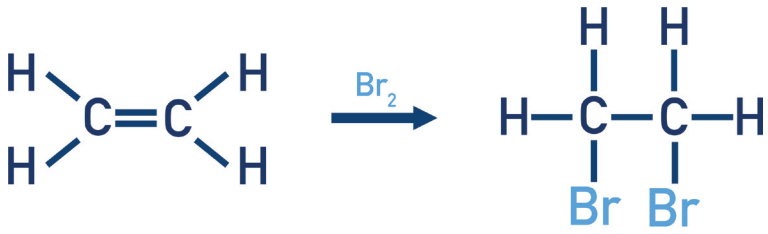
NOTES:

- For unsymetrical alkenes, there will be two possible products from the electrophilic addition.
- Stability of the carbocation intermediate in the mechanism will determine which product will made more readily (**major product**) and which product will be made less readily (**minor product**). *See mechanism.*

Alkenes Addition (Br_2)

REACTANTS: Alkene and Bromine (Br_2)
CONDITIONS: Bromine Liquid (pure Br_2) or Bromine Water (Br_2(aq))
PRODUCT(S): Dibromoalkane
REACTION TYPE: Electrophilic Addition, *Bromination*

REACTION: (example of ethene)



Alkene Dibromoalkane

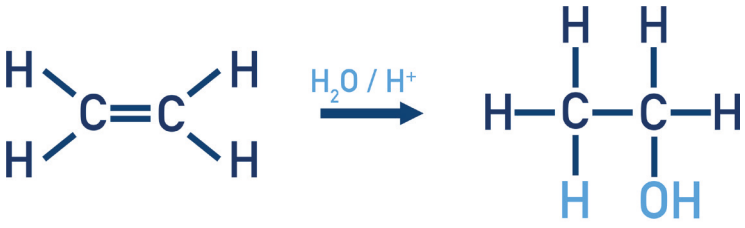
NOTES:

- Double bond in alkene polarises the bromine molecule to form an electrophile ($Br^{\delta+}$) that starts the reaction.
- Reaction can be used to test for the presence of an alkene. A sample is mixed with bromine water, if the bromine water turns colourless (from orange - brown) an alkene is present in the sample.

Alkenes Hydration (to alcohol)

REACTANTS: Alkene and Steam ($H_2O_{(g)}$)
CONDITIONS: Heat and Acid Catalyst (Phosphoric Acid, H_3PO_4)
PRODUCT(S): Alcohol
REACTION TYPE: Electrophilic Addition, *(acid catalysed) Hydration*

REACTION: (example of ethene)



Alkene Alcohol

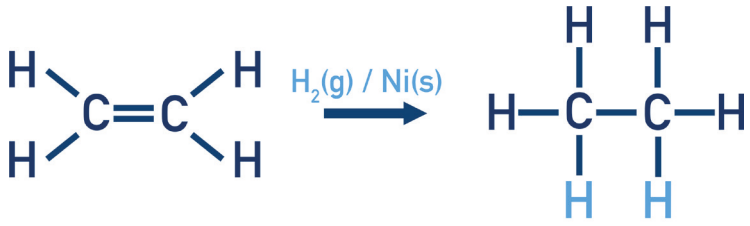
NOTES:

- Acid catalyst is required to form hydroxonium ion (H_3O^+) ion that is able to act as an electrophile to start the reaction.
- For unsymetrical alkenes, there will be two possible products from the electrophilic addition.
- Stability of the carbocation intermediate in the mechanism will determine which product will made more readily (**major product**) and which product will be made less readily (**minor product**).*See mechanism.*

Alkenes Hydrogenation (to alkane)

REACTANTS: Alkene and Hydrogen, H_2
CONDITIONS: Approximately 150°C and Nickel (solid) Catalyst
PRODUCT(S): Alkane
REACTION TYPE: Addition, *Hydrogenation*

REACTION: (example of ethene)



Alkene Alkane

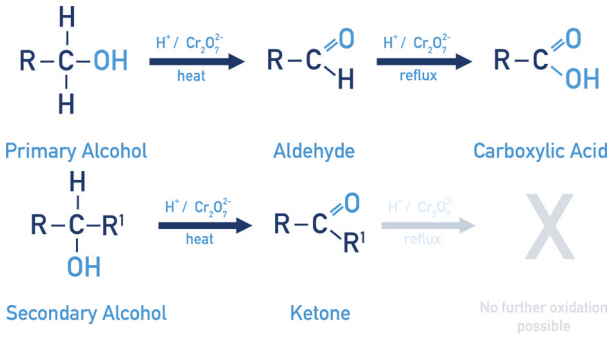
NOTES:

- Hydrogen is 'added' across the double bond - addition reaction and the hydrocarbon becomes saturated (from unsaturated (alkene)).

Alcohols Oxidation

REACTANTS: Alcohol (primary or secondary) and Acidified Dichromate ions ($Cr_2O_7^{2-}$ / H^+)
CONDITIONS: Heat*, Acid Catalyst (sulfuric acid (H_2SO_4))
PRODUCT(S): Aldehyde, Ketone or Carboxylic Acid (see below)
REACTION TYPE: Oxidation

REACTIONS: (example of primary and secondary alcohol)



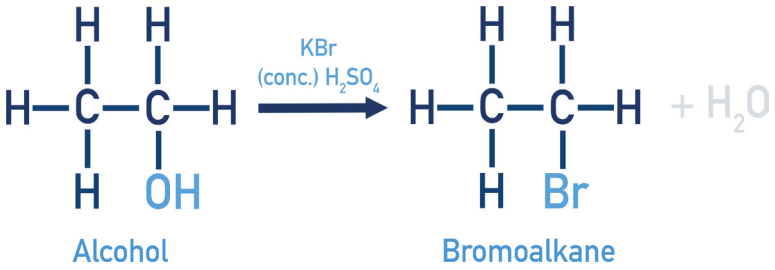
NOTES:

- *Primary alcohols form aldehydes and carboxylic acids when heated with an oxidising agent. To isolate aldehyde, distill aldehyde from reaction mixture as soon as it is formed. To obtain carboxylic acid, heat under reflux to ensure full oxidation of aldehydes already formed.
- Secondary alcohols form ketones and are unable to be further oxidised. Tertiary alcohols are unable to be oxidised at all.
- Oxidising agents can be repesented as [O].

Alcohols Halogenation (KBr)

REACTANTS: Alcohol and 50% (concentrated) H_2SO_4 and Potassium Bromide, KBr
CONDITIONS: (concentrated) H_2SO_4, Warm Temperature (for distillation of product)
PRODUCT(S): Bromoalkane
REACTION TYPE: Halogenation

REACTIONS: (example of ethanol)

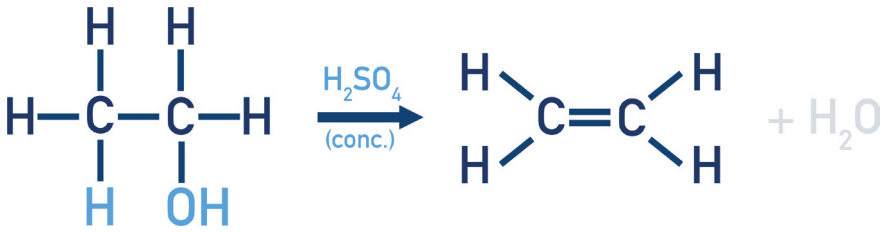


NOTES:
- KBr and H_2SO_4 react together to form HBr that reacts with the alcohol to form the bromoalkane.
- Bromoalkane is isolated from the reaction mixture by distillation.

Alcohols Elimination (to alkenes)

REACTANTS: Alcohol
CONDITIONS: Heat, Acid Catalyst (concentrated H_2SO_4 or concentrated H_3PO_4)
PRODUCT(S): Alkene
REACTION TYPE: Elimination, *dehydration*

REACTION: (example of ethene)



Alcohol Alkene

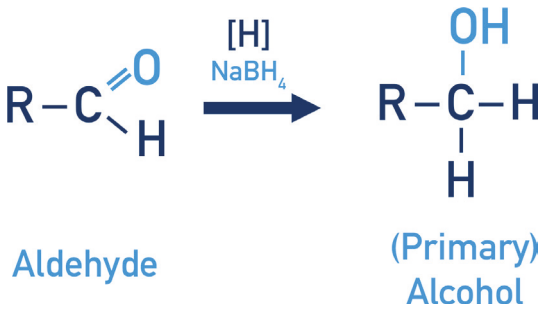
NOTES:

- Acid catalyst provides H^+ ion to start reaction and is reformed at the end when a H^+ ion is released by reacting molecule.
- Water molecule is removed, **dehydration reaction**.

Aldehydes Reduction ($NaBH_4$)

REACTANTS: Aldehyde and $NaBH_4$ (reducing agent)
PRODUCT(S): Primary Alcohol
REACTION TYPE: Reduction

REACTION:



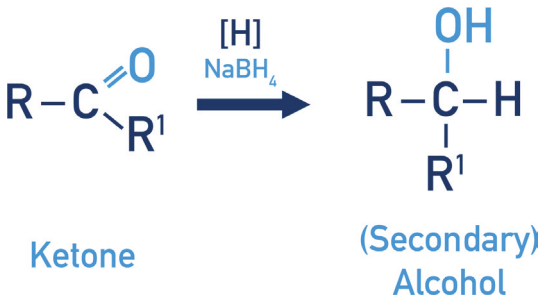
NOTES:

- Aldehydes form **primary alcohols** when reduced.
- $NaBH_4$ is a reducing agent able to provide hydride ($:H^-$) ions that are needed for the reduction of carbonyls.
- The hydrogens added in reduction reactions are often shown as [H].

Ketones Reduction ($NaBH_4$)

REACTANTS: Ketone and $NaBH_4$ (reducing agent)
PRODUCT(S): Secondary Alcohol
REACTION TYPE: Reduction

REACTION:



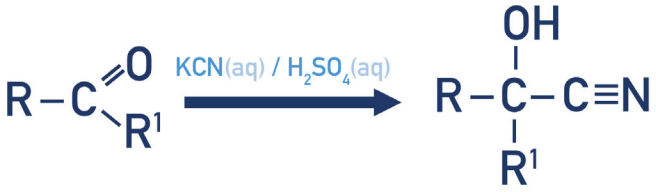
NOTES:

- Ketones form **secondary alcohols** when reduced.
- $NaBH_4$ is a reducing agent able to provide hydride ($:H^-$) ions that are needed for the reduction of carbonyls.
- The hydrogens added in reduction reactions are often shown as [H].

Hydroxynitriles Formation (from carbonyls)

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

REACTION:



Carbonyl Group

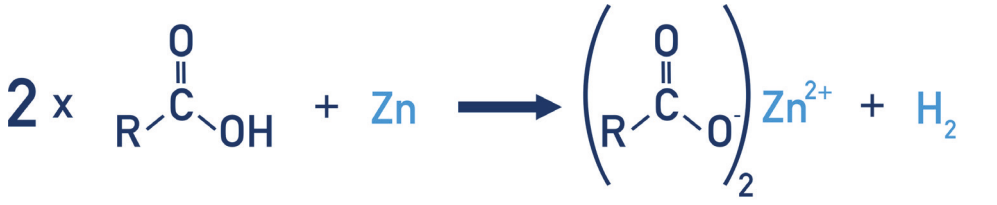
Hydroxynitrile

NOTES:

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

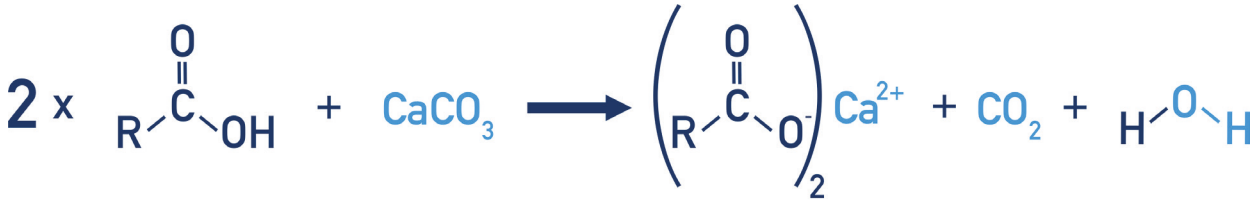
Carboxylic Acids Acid-Base Reactions

Carboxylic acids are able to act as weak acids and react with bases as any weak acid does

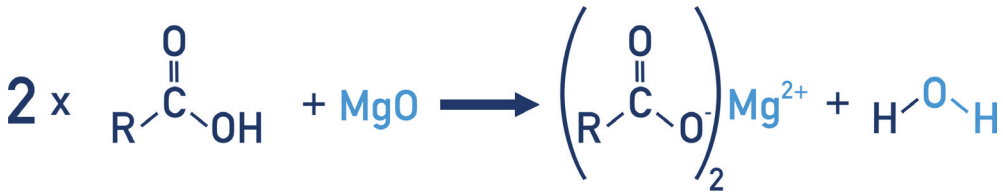


Carboxylic Acid | Metal | Zinc Carboxylate (salt) | Hydrogen

Carboxylic Acid | Alkali | Sodium Carboxylate (salt) | Water



Carboxylic Acid | Metal Carbonate | Calcium Carboxylate (salt) | Carbon Dioxide | Water



Carboxylic Acid | Metal Oxide | Metal Carboxylate (salt) | Water

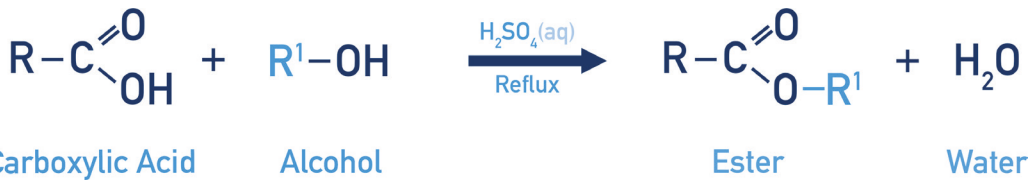
NOTES:

- Salts formed by carboxylic acids are (usually) highly soluble in water and can be a useful source of conjugate bases for making buffer systems.

Esters Esterification (carboxylic acid and alcohol)

REACTANTS: Carboxylic Acid and Alcohol
CONDITIONS: Heat under reflux and (concentrated) Sulfuric Acid (H_2SO_4) catalyst
PRODUCT(S): Ester
REACTION TYPE: Condensation, *Esterification*

REACTION:



Carboxylic Acid | Alcohol | Ester | Water

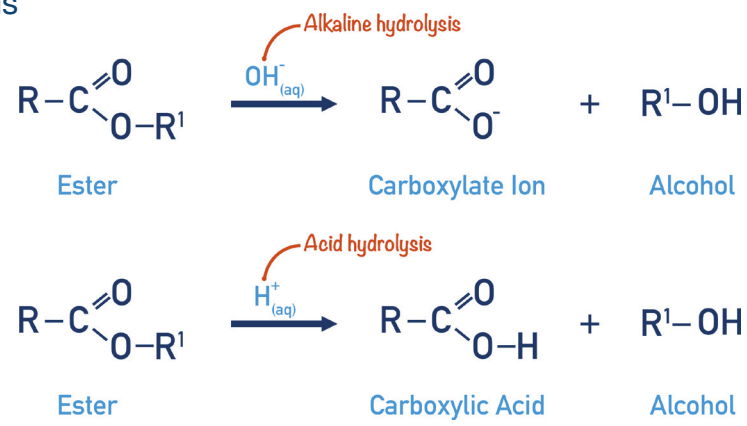
NOTES:

- Reaction is reversible (see hydrolysis of esters), so a (concentrated) acid catalyst is needed to force the position of equilibrium to the formation of ester.

Esters Hydrolysis

REACTANTS: Ester
CONDITIONS: Warm, Aqueous (with dilute acid or alkali)
PRODUCT(S): Carboxylic Acid (or carboxylate salt) and Alcohol
REACTION TYPE: Hydrolysis

REACTION(S):



NOTES:

- If alkaline (OH^-) conditions are used, a carboxylate ion is formed and can be isolated by adding a dilute acid.
- Fats and oils are tri-esters and can be broken down into three fatty acid molecules (carboxylic acids) and one alcohol molecule (glycerol) by hydrolysis.
- Biodisel can be made by the reaction of oil (tri-ester) with methanol in the presence of an acid catalyst, forming methyl esters that can be used as a diesel fuel.

Acyl Chlorides Formation (using $SOCl_2$)

REACTANTS: Carboxylic Acid and Sulfur Dichloride Oxide ($SOCl_2$)
PRODUCT(S): neat $SOCl_2$ (pure liquid $SOCl_2$)

REACTION:

Carboxylic Acid — Acyl Chloride

NOTES:

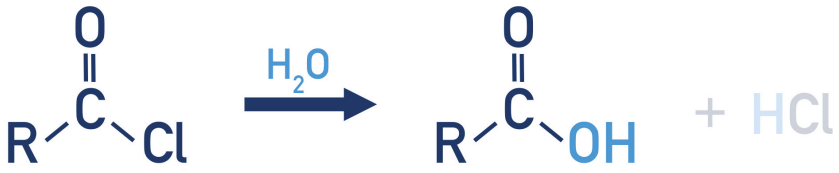
- Sulfur dioxide and hydrogen chloride gas are released as products.

$RCOOH + SOCl_2 \rightarrow RCOCl + SO_2 + HCl$

Acyl Chlorides Addition-Elimination (H_2O)

REACTANTS: Acyl Chloride and H_2O
PRODUCT(S): Carboxylic Acid and HCl
REACTION TYPE: Nucleophilic Addition-Elimination, *Hydrolysis of acyl chloride*

REACTION:



Acyl Chloride Carboxylic Acid

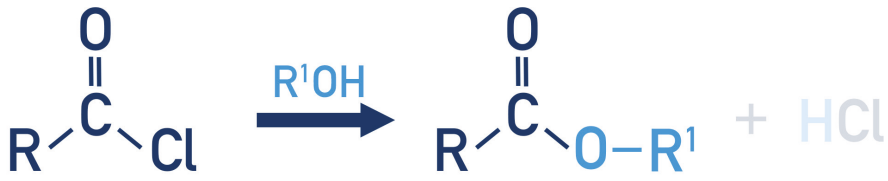
NOTES:

- Acyl chlorides are highly reactive and the reaction is vigorous, with heat given off (exothermic) and fumes of HCl released.

Acyl Chlorides Addition-Elimination (alcohol)

REACTANTS: Acyl Chloride and Alcohol
PRODUCT(S): Ester and HCl
REACTION TYPE: Nucleophilic Addition-Elimination, *Esterification*

REACTION:



Acyl Chloride Ester

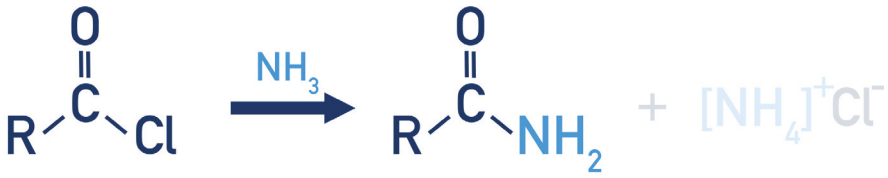
NOTES:

- Ester formed (esterification) has a sweet, fruity smell.

Acyl Chlorides Addition-Elimination (NH_3)

REACTANTS: Acyl Chloride and Ammonia
PRODUCT(S): Amide and HCl
REACTION TYPE: Nucleophilic Addition-Elimination

REACTION:



Acyl Chloride Amide

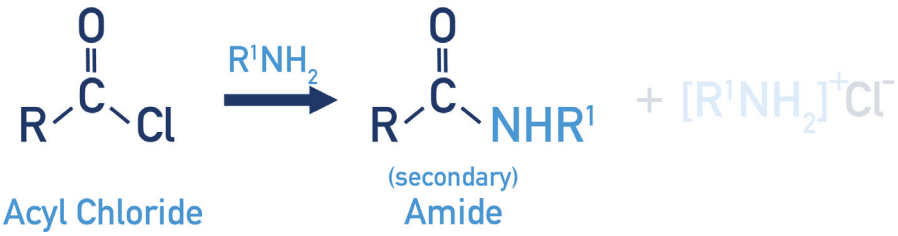
NOTES:

- Ammonia produces a **primary amide** and ammonium chloride salt when reacted with acyl chlorides.
- Primary amines produce a **secondary amide** and an alkyl ammonium chloride salt when reacted with acyl chlorides.
- Secondary amines produce a **tertiary amide** and an alkyl ammonium chloride salt when reacted with acyl chlorides.

Acyl Chlorides Addition-Elimination (amine)

REACTANTS: Acyl Chloride and Amine (primary)
PRODUCT(S): (Secondary) Amide and Alkyl Ammonium Chloride
REACTION TYPE: Nucleophilic Addition-Elimination

REACTION:



Acyl Chloride

(secondary) Amide

NOTES:

- Primary amines produce a **secondary amide** and an alkyl ammonium chloride salt when reacted with acyl chlorides.
- Secondary amines produce a **tertiary amide** and an alkyl ammonium chloride salt when reacted with acyl chlorides.

Benzene Bromination (adding Br_2)

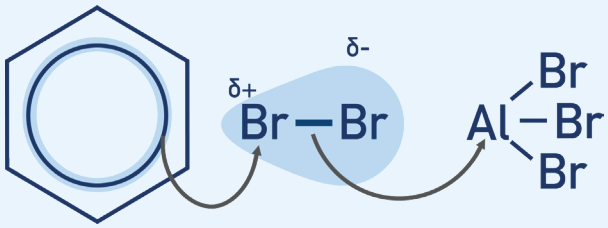
REACTANTS: Benzene and Bromine (Br_2)
CONDITIONS: Halogen Carrier ($AlBr_3$ or Fe)
PRODUCT(S): Bromobenzene
REACTION TYPE: Electrophilic Substitution, *Bromination*

REACTION: (example of benzene)

Benzene Bromobenzene

NOTES:

- The delocalised electron system in benzene is unable to polarise the bromine molecule enough to form an electrophile.
- A halogen carrier ($AlBr_3$ or Fe) is used to form the bromine electrophile.

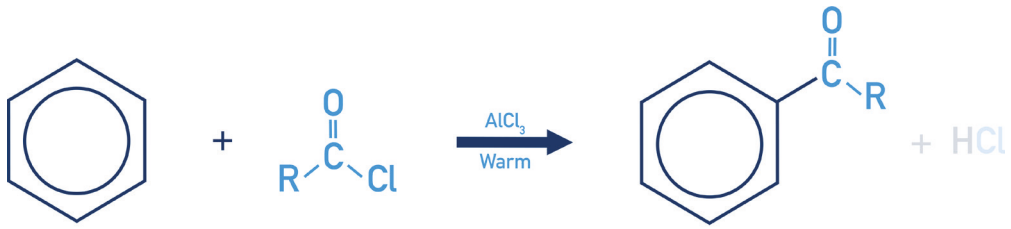


- H^+ ion removed from benzene ring combines with Br from halogen carrier intermediate, $[AlBr_4]^-$ to form HBr and reform the halogen carrier ($AlBr_3$)

Benzene Acylation (with acyl chlorides)

REACTANTS: Benzene and Acyl Chloride
CONDITIONS: Warm and $AlCl_3$ catalyst
PRODUCT(S): (Aromatic) Ketone
REACTION TYPE: Electrophilic Substitution, *Acylation (Friedel Crafts)*

REACTION: (example of benzene)

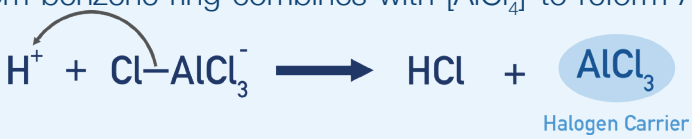


Benzene (Aromatic) Ketone

NOTES:

- Acylium (RCO^+) ion is formed by reacting an acyl chloride with a halogen carrier ($AlCl_3$).

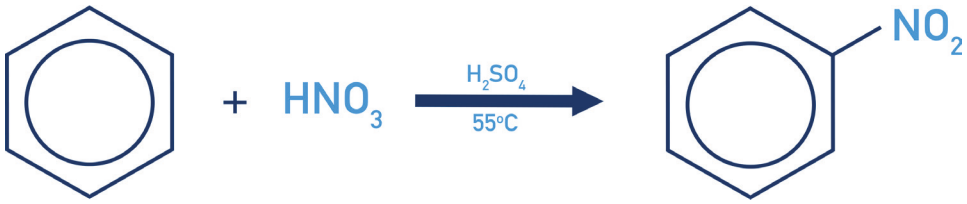
- H^+ ion removed from benzene ring combines with $[AlCl_4]^-$ to reform $AlCl_3$ catalyst and form HCl.



Benzene Nitration (adding NO_2)

REACTANTS: Benzene and (concentrated) Nitric Acid (HNO_3)
CONDITIONS: (Concentrated) Sulfuric Acid (H_2SO_4)
PRODUCT(S): Nitrobenzene
REACTION TYPE: Electrophilic Substitution, *Nitration*

REACTION: (example of benzene)



Benzene — Nitrobenzene

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.

Benzene Alkylation (with halogenoalkanes)

REACTANTS: Benzene and Halogenoalkane
CONDITIONS: Warm and $AlCl_3$ (or $AlBr_3$) catalyst
PRODUCT(S): Alkylbenzene
REACTION TYPE: Electrophilic Substitution, *Alkylation (Friedel-Crafts)*

REACTION: (example of benzene)

Benzene — Alkylbenzene

NOTES:

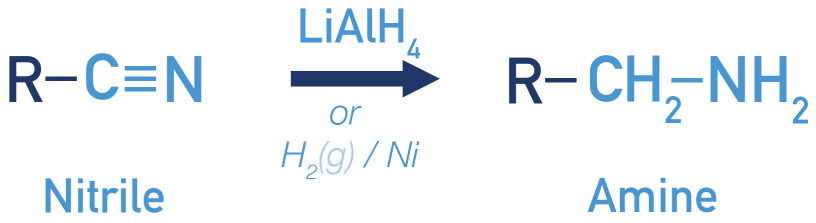
- Alkyl (R^+) ion is formed by reacting an acyl chloride with a halogen carrier ($AlCl_3$).

- H^+ ion removed from benzene ring combines with $[AlCl_4]^-$ to reform $AlCl_3$ catalyst and form HCl.

Nitriles Reduction (to form primary amine)

REACTANTS: Nitrile and Reducing Agent - $LiAlH_4$, or Hydrogen gas ($H_2(g)$)
CONDITIONS: Dry ether* (if using $LiAlH_4$), Nickel catalyst (if using $H_2(g)$)
PRODUCT(S): Amine
REACTION TYPE: Reduction, *Hydrogenation*

REACTION:



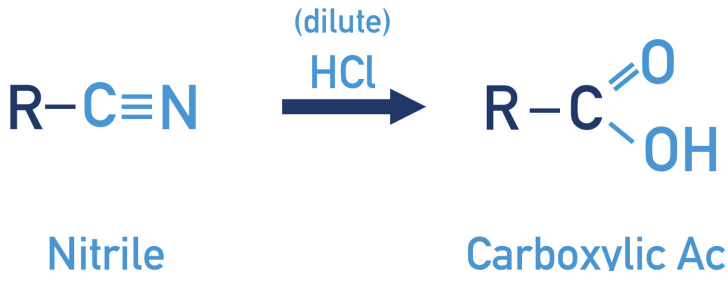
NOTES:

- If $H_2(g)$ and a nickel catalyst is used, the reaction is an example of catalytic hydrogenation.
- *Dry ether must be used with $LiAlH_4$ ($LiAlH_4$ reacts violently with water). To obtain the amine as a final product, dilute acid must be added to the inital product from reduction.

Nitriles Acid Hydrolysis (to form carboxylic acids)

REACTANTS: Nitrile and (dilute) Hydrochloric Acid (HCl)
CONDITIONS: Heat under reflux
PRODUCT(S): Carboxylic Acid and Ammonium Chloride
REACTION TYPE: Hydrolysis

REACTION:



Nitrile Carboxylic Acid

NOTES:

- Full reaction:

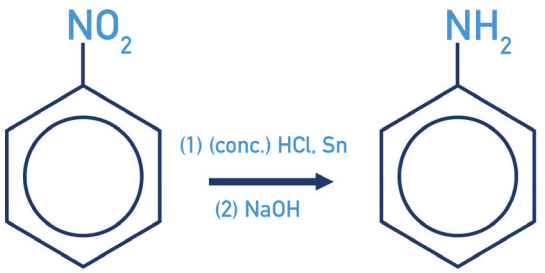
$$\mathbf{RCN + 2H_2O + HCl \rightarrow RCOOH + [NH_4]^+Cl^-}$$

- Nitriles can also be hydrolysed in alkaline conditions (heated under reflux) using sodium hydroxide, forming the sodium carboxylate salt of the carboxylic acid.

Nitroarenes Reduction (to form aromatic amines)

REACTANTS: Nitroarene and (concentrated) Hydrochloric Acid (HCl), *followed by NaOH*
CONDITIONS: Tin catalyst
PRODUCT(S): Aromatic Amine
REACTION TYPE: Reduction

REACTION: (example of nitrobenzene)



Nitroarene Phenylamine

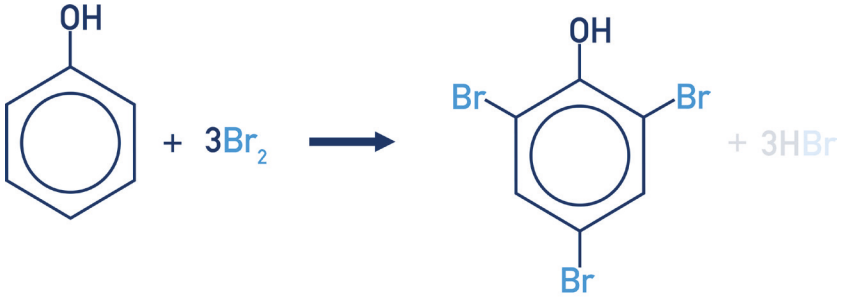
NOTES:

- When reacted with concentrated HCl, the nitroarene will form an ammonium ion -NH_3^+. The aromatic amine can be obtained by adding dilute sodium hydroxide (to form -NH_2).

Phenol Bromination (Br_2)

REACTANTS: Phenol and Bromine water ($Br_2(aq)$)
PRODUCT(S): 2,4,6-tribromopenol
REACTION TYPE: Electrophilic Substitution, *Bromination*

REACTION: (example of phenol)



Phenol — 2,4,6-tribromophenol

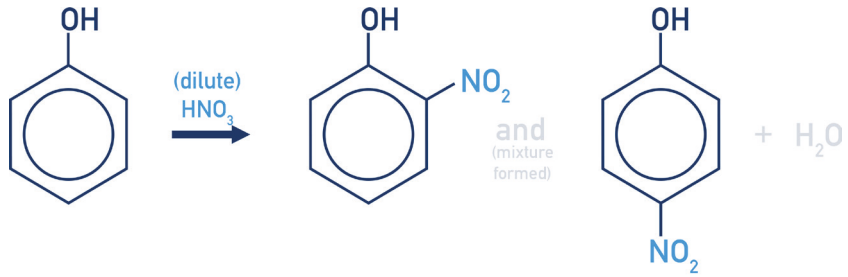
NOTES:

- Bromine water changes from orange-brown to colourless and a white precipitate forms.
- Unlike with benzene, no halogen carrier catalyst is needed for the bromination of phenol. This is due to the increased electron density in the delocalised electron ring (from the -OH group), making phenol more reactive than benzene.

Phenol Nitration (using dilute nitric acid, HNO_3)

REACTANTS: Phenol and dilute Nitric Acid (HNO_3)
PRODUCT(S): 2-nitrophenol and 4-nitrophenol (mixture)
REACTION TYPE: Electrophilic Substitution, *Nitration*

REACTION: (example of phenol)



Phenol | 2-nitrophenol | 4-nitrophenol

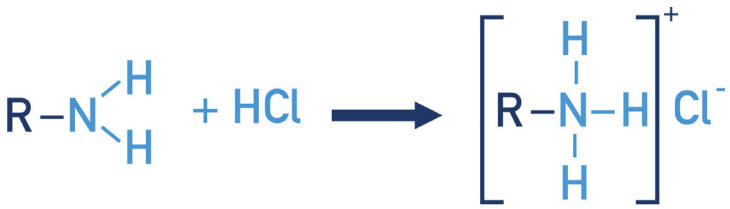
NOTES:

- Unlike with benzene, no sulfuric acid (H_2SO_4) catalyst is needed for the bromination of phenol. This is due to the increased electron density in the delocalised electron ring (from the -OH group) making phenol more reactive than benzene.
- If concentrated nitric acid is used, three NO_2 groups can be substituted, forming 2,4,6-trinitrophenol.

Amines Acting as Bases (with acids)

REACTANTS: Amine and Acid
PRODUCT(S): Alkyl Ammonium Salt
REACTION TYPE: Acid-Base

REACTION:



Amine Acid Alkyl ammonium salt

NOTES:

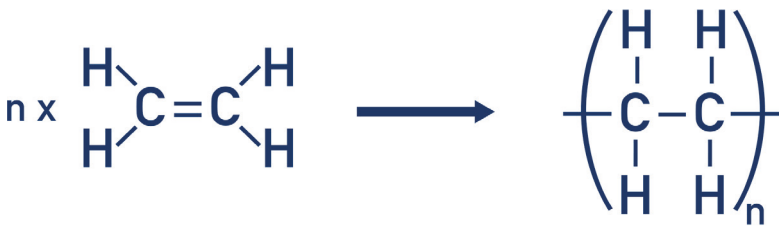
- Nitrogen atom in amine has lone pair of electrons that can act as a base and accept a H^+ ion in an acidic solution, forming an alkyl ammonium salt (with the negative ion from the acid).
- Butylamine with hydrochloric acid:

$$CH_3CH_2CH_2CH_2NH_2 + HCl \rightarrow [CH_3CH_2CH_2CH_2NH_3]^+Cl^-$$ *(butylammonium chloride)*

Polymers Addition (from alkenes)

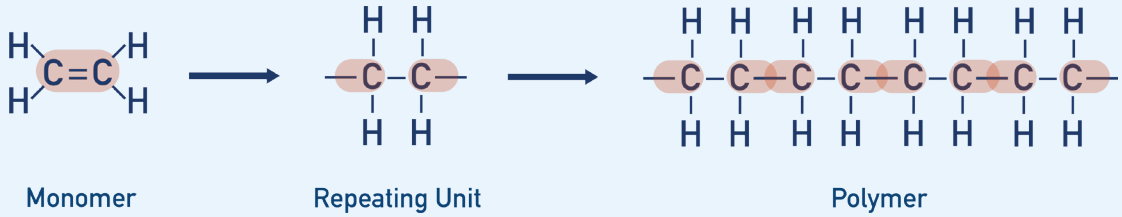
REACTANTS: Alkene
PRODUCT(S): Poly(alkene)
REACTION TYPE: Addition Polymerisation

REACTION: (example of ethene)



NOTES:

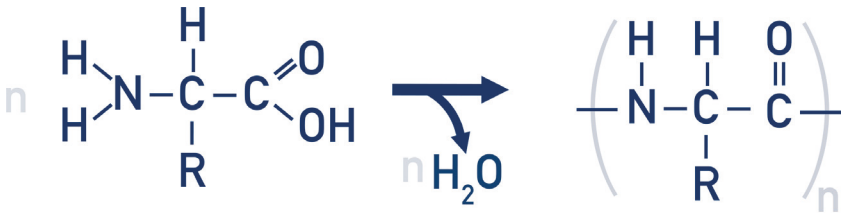
- The carbon-carbon double bond in the alkene breaks, allowing each carbon atom to form a new bond (with another carbon atom from another molecule).
- The alkenes that form a polymer are called **monomers**.
- The polymer is made up of **repeating units**.



Amino Acids Condensation Polymerisation (form proteins)

REACTANTS: Amino Acids
PRODUCT(S): Polyamide (polypeptide)
REACTION TYPE: Condensation Polymerisation

REACTION:



Amino Acid Polyamide

NOTES:

- Polymer formed is a polyamide, often referred to as a polypeptide in biology.
- Polyamide chains formed by amino acids are used in nature to make up proteins.
- DNA is a 'code' used by organisms to give the correct amino acid sequence for a particular protein. A section of DNA that codes for a given protein is called a gene.