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

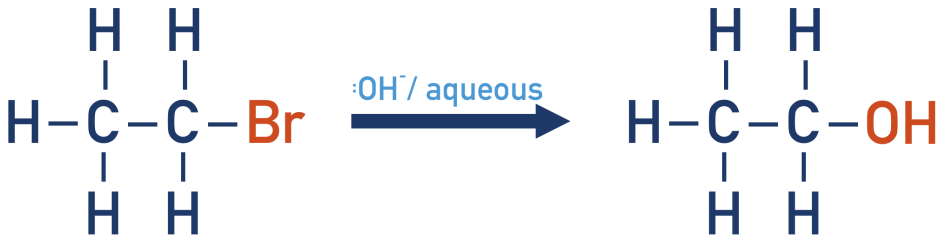
NOTES:

- 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

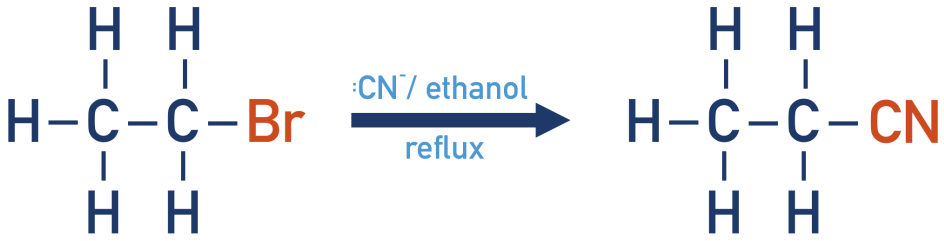
NOTES:

- 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

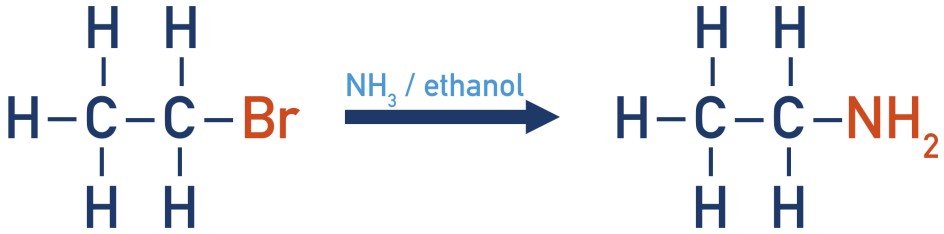
NOTES:

- 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.

Halogenoalkanes Substitution (NH_3)

REACTANTS: Halogenoalkane and Ammonia (NH_3)
CONDITIONS: Heat*, Ethanolic (ethanol as the solvent, **no water present**)
PRODUCT(S): Amine and Ammonium Halide Salt
REACTION TYPE: Nucleophilic Substitution

REACTION: (example of bromoethane)



Halogenoalkane — Amine

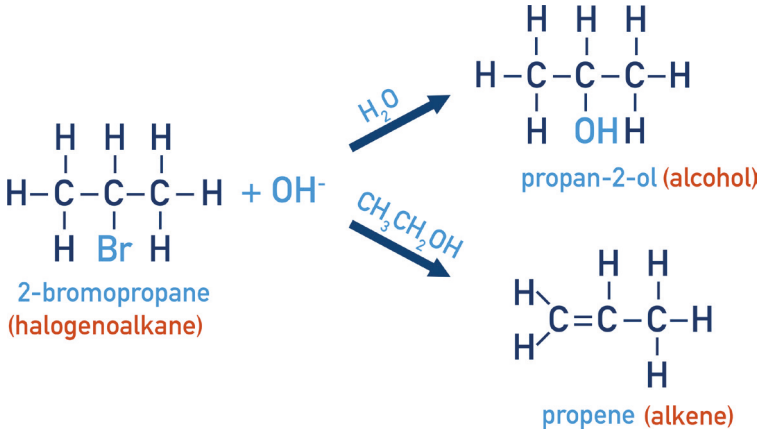
NOTES:

- Reaction must be carried out in **ethanolic conditions (in ethanol, no water present), otherwise an alcohol is likely to form** rather than the amine.
- *A sealed container (to stop ammonia escaping) containing reactants is heated.
- The amine formed in the reaction is a stronger base than ammonia and an ammonium-alkyl $[RNH_3]^+$ salt may be formed. The amine can be obtained by adding sodium hydroxide to the mixture - forcing the alkyl-ammonium ion to 'release' a H^+ ion and become a neutral molecule.
- 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).

Halogenoalkanes Substitution and Elimination (OH^-)

REACTANTS: Halogenoalkane and Potassium Hydroxide (for OH^- ions)
CONDITIONS: Heat under reflux, Ethanolic or Aqueous*
PRODUCT(S): Alcohol **and** Alkene (possible mixture of both)
REACTION TYPE: Nucleophilic Substitution **and** Elimination

REACTION(S): (example of 2-bromo-propane)



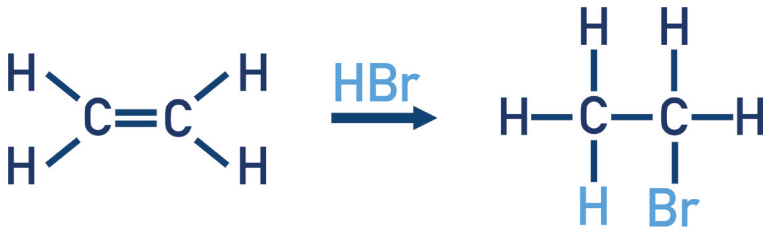
NOTES:

- Halogenoalkanes can react with hydroxide (OH^-) ions in both substitution and elimation reactions.
- If **substitution occurs an alcohol is formed,** whereas if **elimination occurs an alkene is formed.**
- The solvent used can help ensure more of one product is formed than the other, although final product mixture can still contain both the alcohol and alkene.
- If a hot **aqueous solvent is used, more alcohol forms.**
- If a hot **ethanolic solvent is used, more alkene forms.**
- Primary alcohols are **more likely to undergo substitution** - tertiary alcohols are **more likely to undergo elimination**. Secondary alcohols can undergo both substitution and elimination.
- *Higher temperatures and a more concentrated solution of hydroxide ions favour elimination.*

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

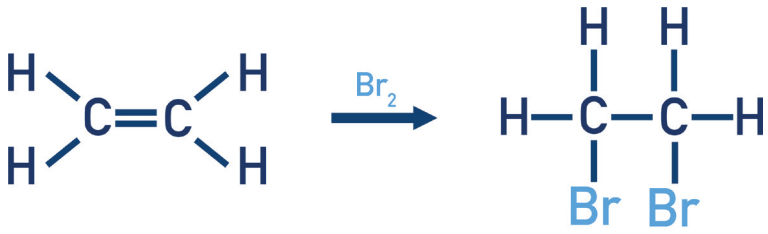
NOTES:

- 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

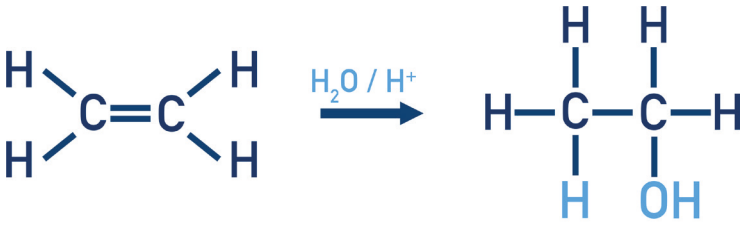
NOTES:

- 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

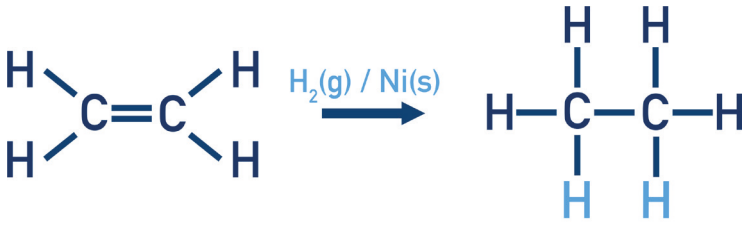
NOTES:

- 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

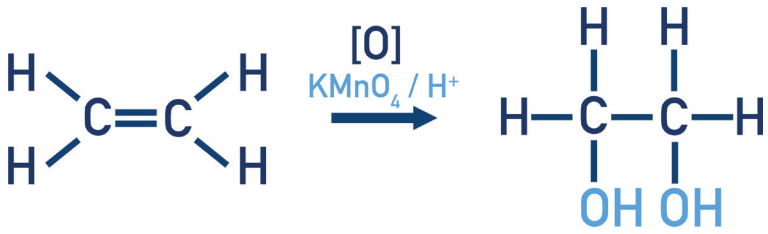
NOTES:

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

Alkenes Oxidation (to form diol)

REACTANTS: Alkene and (dilute) Potassium Manganate (VII)
CONDITIONS: Cold Temperature, Acidic Conditions
PRODUCT(S): Diol
REACTION TYPE: Oxidation

REACTION: (example of ethene)



Alkene Diol

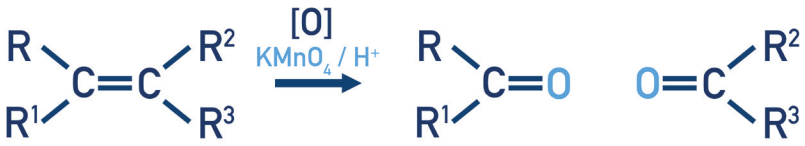
NOTES:

- Oxidation reaction must be carried out in cold temperature with dilute potassium manganate to ensure the diol doesn't get further oxidised and split in two (forming two carbonyl containing molecules).
- Colour change of the acidified potassium mangangante (VII) - (***purple to colourless***), can be used as a test to show a double bond is present (although the bromine water test is simpler and more specific).

Alkenes Oxidation (breaking C=C double bond)

REACTANTS: Alkene and (concentrated) Potassium Manganate (VII)
CONDITIONS: Hot Temperature, Acidic Conditions
PRODUCT(S): Two Carbonyl Molecules (split C=C double bond)
REACTION TYPE: Oxidation

REACTION:



Alkene

Ketones (or carboxylic acids, depending on R groups)

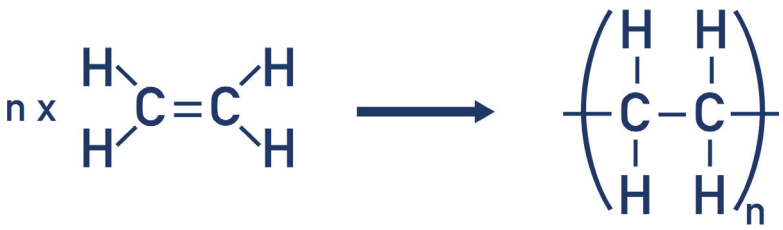
NOTES:

- If concentrated potassium manganate (VII) and a high temperature is used, the carbon double bond in the alkene is broken completely and two new carbonyl groups form (each on a new molecule).
- Depending on the R groups of the original alkene, carboxylic acids can form (if one of the R groups is H) as an aldehyde formed would be further oxidised to a carboxylic acid.

Polymers Addition (from alkenes)

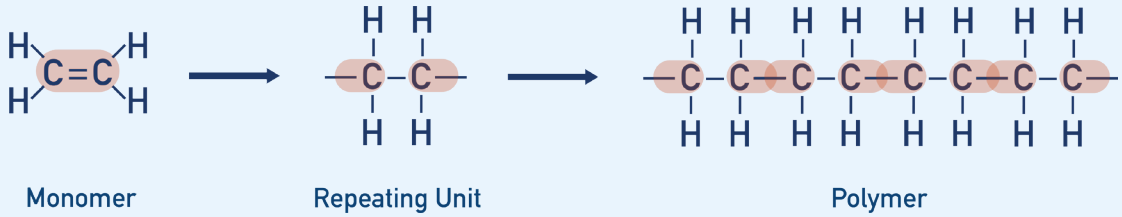
REACTANTS: Alkene
PRODUCT(S): Poly(alkene)
REACTION TYPE: Addition Polymerisation

REACTION: (example of ethene)



NOTES:

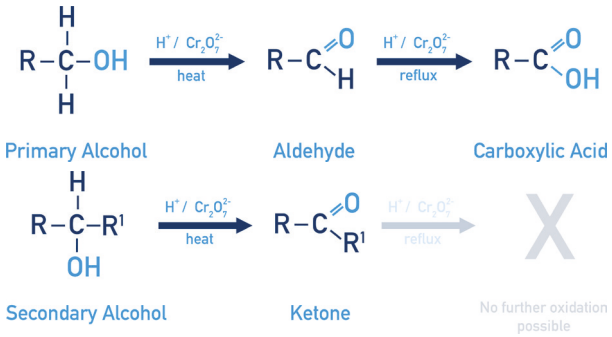
- The carbon-carbon double bond in the alkene breaks, allowing each carbon atom to form a new bond (with another carbon atom from another molecule).
- The alkenes that form a polymer are called **monomers**.
- The polymer is made up of **repeating units**.



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)



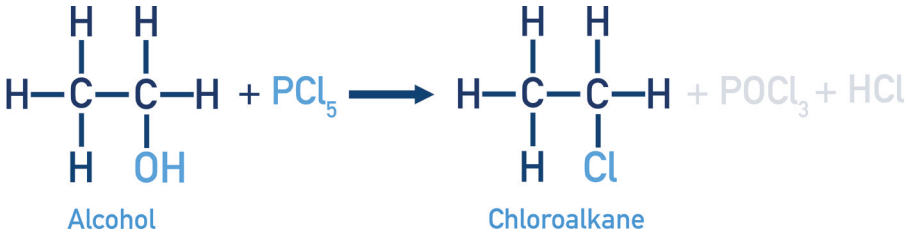
NOTES:

- *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 (PCl_5)

REACTANTS: Alcohol and (solid) Phosphorus (V) Pentachloride (PCl_5)
CONDITIONS: Pure alcohol (no water must be present)
PRODUCT(S): Chloroalkane and HCl (white fumes)
REACTION TYPE: Halogenation

REACTIONS: (example of ethanol)



Alcohol Chloroalkane

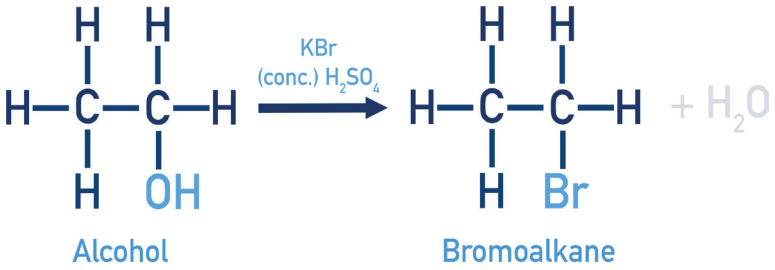
NOTES:

- PCl_5 reacts vigorously with -OH groups, producing white misty fumes of HCl. Due to this, the sample of alcohol being halogenated must be pure containing no water or other molecules with an -OH group.
- The reaction can be used to test for an alcohol (positive result is observation of misty white fumes).

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)



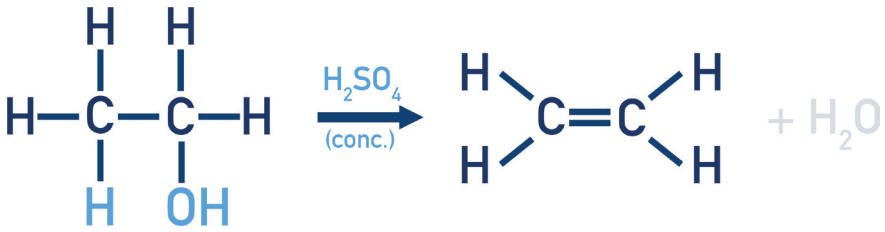
NOTES:

- 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**.

Alcohols With Sodium, Na

REACTANTS: Alcohol and Sodium
PRODUCT(S): Alkoxide and Sodium Ion (Na^+)

REACTION: (example of ethanol)

Alcohol → 'Alkoxide'

NOTES:

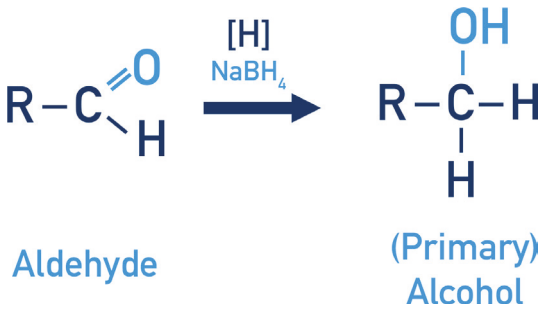
- Alcohol reacts in a similar way with sodium metal as water. Hydrogen gas is released, the sodium metal becomes a positively charged ion (Na^+) and the ROH group becomes a negatively charged 'alkoxide' ion ($RO:^-$).
- Ethanol reacts with sodium metal to form sodium ethoxide:

$$2CH_3CH_2OH + 2Na \rightarrow 2CH_3CH_2O^-Na^+ + H_2$$

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:

Ketone

(Secondary) Alcohol

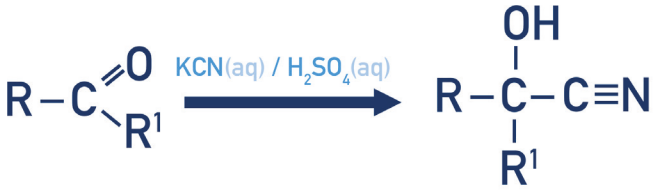
NOTES:

- 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

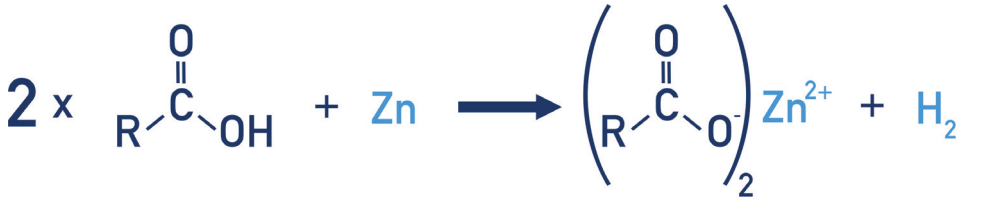
Hydroxynitrile

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.

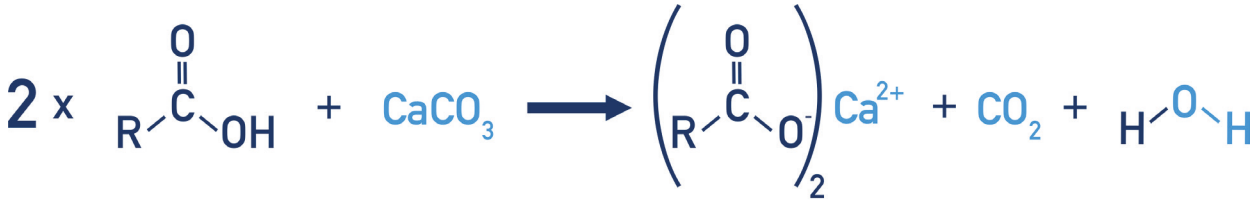
Carboxylic Acids Acid-Base Reactions

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

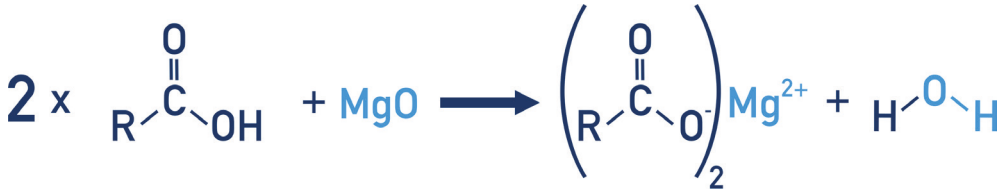


Carboxylic Acid | Metal | Zinc Carboxylate (salt) | Hydrogen

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

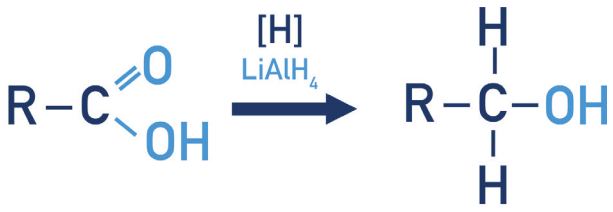
NOTES:

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

Carboxylic Acids Reduction (to alcohols using $LiAlH_4$)

REACTANTS: Carboxylic Acid and $LiAlH_4$
CONDITIONS: Dry ether (room temperature)
PRODUCT(S): Primary Alcohol
REACTION TYPE: Reduction

REACTION:



Carboxylic Acid → (primary) Alcohol

NOTES:

- $LiAlH_4$ is used as the reducing agent as $NaBH_4$ isn't powerful enough to reduce the carboxylic acid.
- Reducing agent can be represented as [H] when writing the reaction:

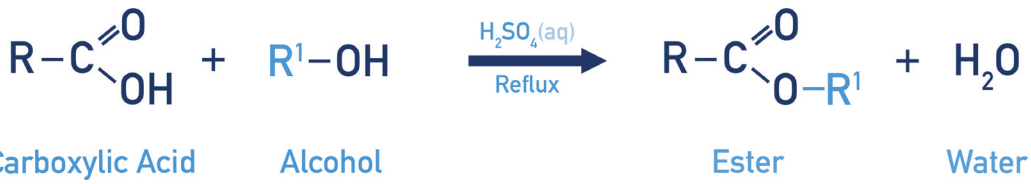
$$RCOOH + 4[H] \rightarrow RCH_2OH + H_2O$$

- Reaction must be carried out in dry ether (no water present) as $LiAlH_4$ reacts vigorously with water.

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

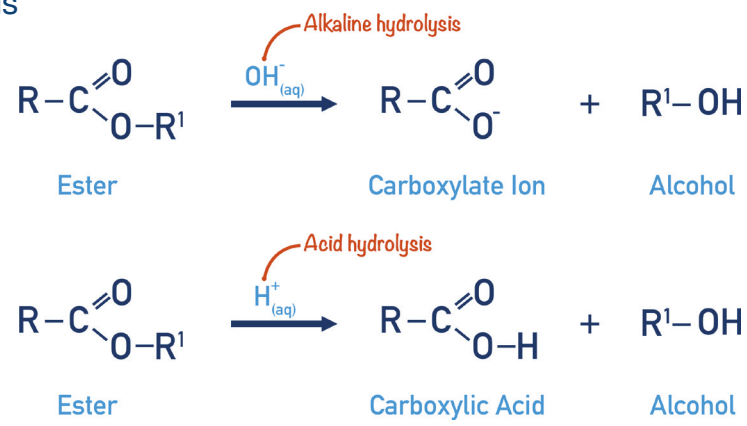
NOTES:

- 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.

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:

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

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