

## 6. Module 2 Organic Chemistry

### Alcohols

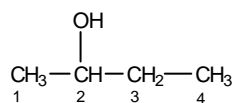
General formula alcohols  $C_nH_{2n+1}OH$

#### Naming Alcohols

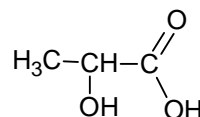
These have the ending **-ol** and if necessary the position number for the OH group is added between the name stem and the **-ol**

If the compound has an **-OH** group in addition to other functional groups that need a suffix ending then the OH can be named with the prefix **hydroxy-**:

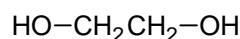
If there are two or more **-OH** groups then di, tri are used. Add the 'e' on to the stem name though



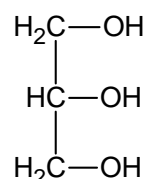
Butan-2-ol



2-hydroxypropanoic acid



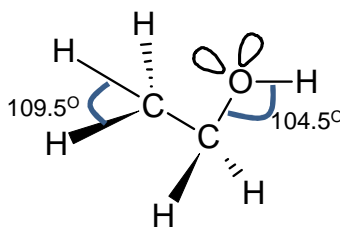
Ethane-1,2-diol



propane-1,2,3-triol

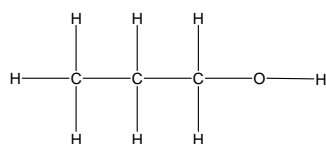
#### Bond angles in Alcohols

All the H-C-H bonds and C-C-O are  $109.5^\circ$  (tetrahedral shape), because there are 4 bond pairs of electrons repelling to a position of minimum repulsion.



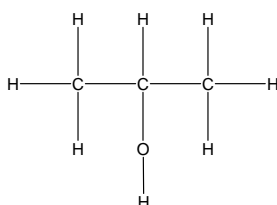
The H-O-C bond is  $104.5^\circ$  (bent line shape), because there are 2 bond pairs of electrons and 2 lone pairs repelling to a position of minimum repulsion. Lone pairs repel more than bond pairs so the bond angle is reduced.

#### Different types of alcohols



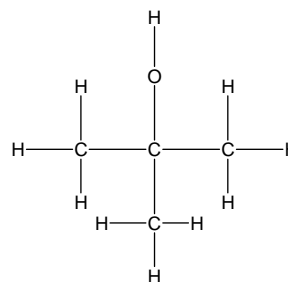
Propan-1-ol  
Primary

Primary alcohols are alcohols where 1 carbon is attached to the carbon adjoining the oxygen



Propan-2-ol  
Secondary

Secondary alcohols are alcohols where 2 carbon are attached to the carbon adjoining the oxygen

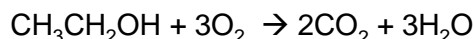


methylpropan-2-ol  
Tertiary

Tertiary alcohols are alcohols where 3 carbon are attached to the carbon adjoining the oxygen

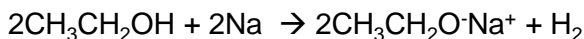
## 1. Combustion of Alcohols

Alcohols combust with a clean flame



## 2. Reaction of Alcohols with Sodium

Sodium reacts with alcohols



This reaction can be used as a test for alcohols

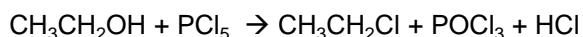
### Observations:

- effervescence,
- the mixture gets hot,
- sodium dissolves,
- a white solid is produced.

## 3. Substitution reactions of Alcohols to form Halogenoalkanes

Various halogenating compounds can be used to substitute the -OH group for a halogen

### Reaction with phosphorous (V) halide

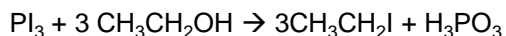


This reaction with  $\text{PCl}_5$  (phosphorous(v)chloride) can be used as a test for alcohols. You would observe misty fumes of HCl produced.

$\text{PCl}_5$  /  $\text{PCl}_3$  / conc HCl /  $\text{SOCl}_2$  / mixture of NaCl +  $\text{H}_2\text{SO}_4$  can all be used for substituting a Cl

For Br and I it is best to use  $\text{PI}_5$ ,  $\text{PI}_3$  and Br equivalents. It is not suitable to use NaBr, or NaI +  $\text{H}_2\text{SO}_4$  to produce HBr or HI because the sulphuric acid will oxidise the hydrogen halides to other products

### Reaction with phosphorous (III) halide



The **phosphorous (III) halide** can also be produced in situ by reacting red phosphorus and the halogen.

## 4. Oxidation reactions of the alcohols

Potassium dichromate  $\text{K}_2\text{Cr}_2\text{O}_7$  is an oxidising agent that causes alcohols to oxidise.

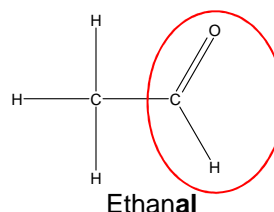
The exact reaction, however, depends on the type of alcohol, i.e. whether it is primary, secondary, or tertiary, and on the conditions.

### Partial Oxidation of Primary Alcohols

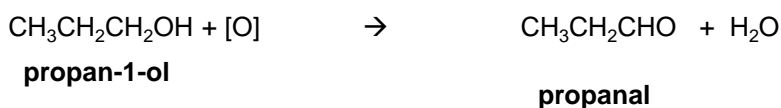
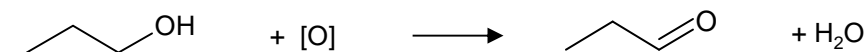
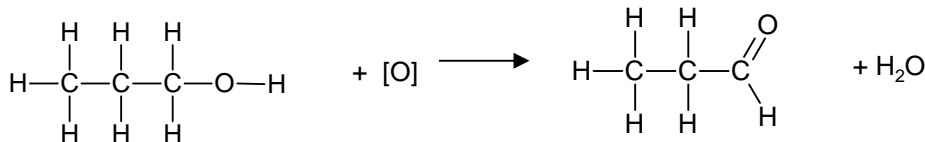
**Reaction:** primary alcohol  $\rightarrow$  aldehyde

**Reagent:** potassium dichromate (VI) solution and dilute sulphuric acid.

**Conditions:** (use a limited amount of dichromate) warm gently and **distil** out the aldehyde as it forms:



An aldehyde's name ends in **-al**  
It always has the C=O bond on the first carbon of the chain so it does not need an extra number



Observation: the orange dichromate ion ( $\text{Cr}_2\text{O}_7^{2-}$ ) reduces to the green  $\text{Cr}^{3+}$  ion

Write the oxidation equations in a simplified form using [O] which represents O from the oxidising agent

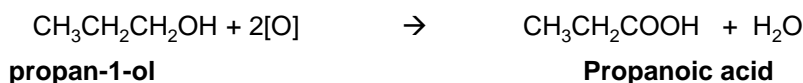
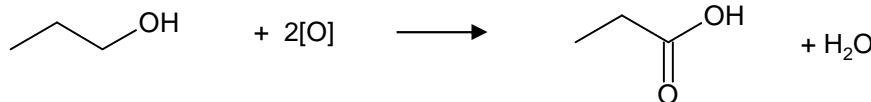
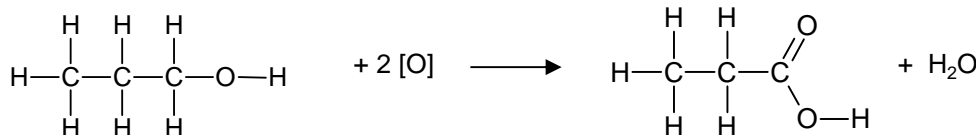
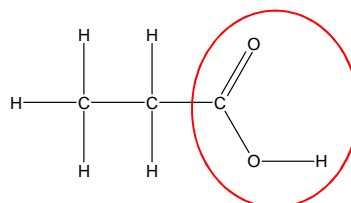
When writing the formulae of aldehydes in a condensed way write **CHO** and not COH e.g.  $\text{CH}_3\text{CH}_2\text{CHO}$

## Full Oxidation of Primary Alcohols

**Reaction:** primary alcohol → carboxylic acid

**Reagent:** potassium dichromate(VI) solution and dilute sulphuric acid

**Conditions:** use an excess of dichromate, and **heat under reflux**: (distill off product after the reaction has finished)



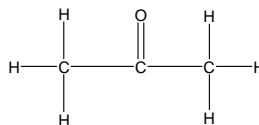
Observation: the orange dichromate ion ( $\text{Cr}_2\text{O}_7^{2-}$ ) reduces to the green  $\text{Cr}^{3+}$  ion

## Oxidation of Secondary Alcohols

**Reaction:** secondary alcohol → ketone

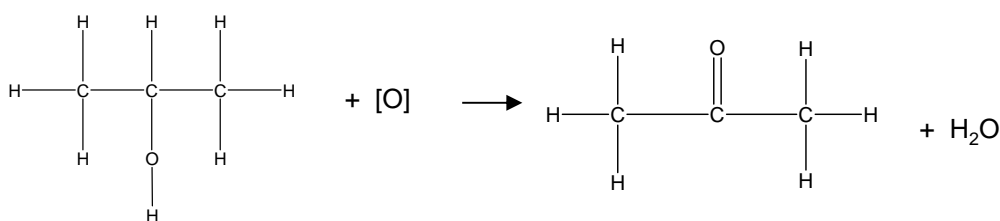
**Reagent:** potassium dichromate(VI) solution and dilute sulphuric acid.

**Conditions:** heat under reflux



Ketones end in **-one**

When ketones have 5C's or more in a chain then it needs a number to show the position of the double bond. E.g. pentan-2-one



propan-2-ol

Propanone

Observation: the orange dichromate ion ( $\text{Cr}_2\text{O}_7^{2-}$ ) reduces to the green  $\text{Cr}^{3+}$  ion

There is no further oxidation of the ketone under these conditions.

**Tertiary alcohols** cannot be oxidised at all by potassium dichromate: This is because there is no hydrogen atom bonded to the carbon with the OH group

## Distinguishing between Aldehydes and Ketones

The fact that aldehydes can be further oxidised to carboxylic acids whereas ketones cannot be further oxidised is the chemical basis for tests that are commonly used to distinguish between aldehydes and ketones

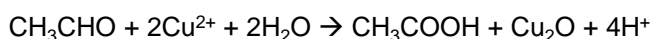
### Fehling's (Benedict's) solution

**Reagent:** Fehling's Solution containing blue  $\text{Cu}^{2+}$  ions.

**Conditions:** heat gently

**Reaction:** **aldehydes only** are oxidised by Fehling's solution into a carboxylic acid and the copper ions are reduced to copper(I) oxide

**Observation:** **Aldehydes**: Blue  $\text{Cu}^{2+}$  ions in solution change to a red precipitate of  $\text{Cu}_2\text{O}$ . **Ketones do not react**



The presence of a carboxylic acid can be tested by addition of sodium carbonate. It will fizz and produce carbon dioxide

## Organic techniques

### Distillation

In general used as separation technique to separate an organic product from its reacting mixture. Need to collect the distillate of the approximate boiling point range of the desired liquid.

#### Classic AS reaction using distillation

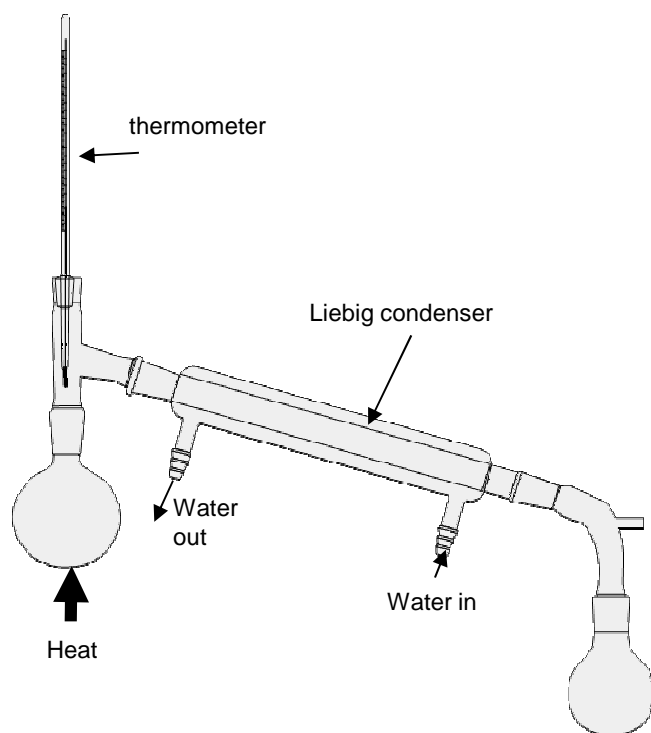
**Reaction:** primary alcohol  $\rightarrow$  aldehyde

**Reagent:** potassium dichromate (VI) solution and dilute sulphuric acid.

**Conditions:** use a limited amount of dichromate and **warm gently and distil** out the aldehyde as it forms [This prevents further oxidation to the carboxylic acid]

#### Observation

Orange dichromate solution changes to green colour of  $\text{Cr}^{3+}$  ions



Note the bulb of the thermometer should be at the T junction connecting to the condenser to measure the correct boiling point

Note the water goes in the bottom of the condenser to go against gravity. This allows more efficient cooling and prevents back flow of water.

### Reflux

Reflux is used when heating organic reaction mixtures for long periods. The condenser prevents organic vapours from escaping by condensing them back to liquids.

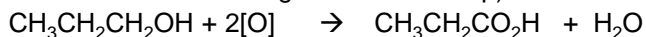
**Never seal the end of the condenser** as the build up of gas pressure could cause the apparatus to explode. This is true of any apparatus where volatile liquids are heated including the distillation set up

#### Classic AS reaction using reflux

**Reaction:** primary alcohol  $\rightarrow$  carboxylic acid

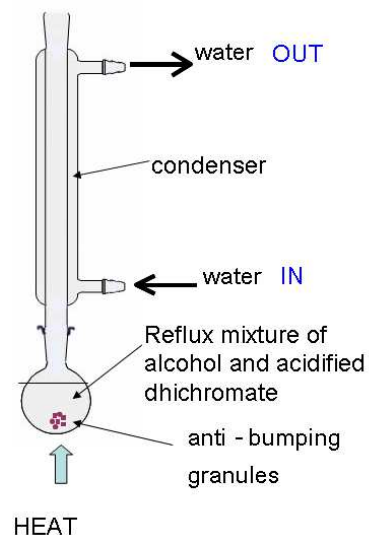
**Reagent:** potassium dichromate(VI) solution and dilute sulphuric acid

**Conditions:** use an excess of dichromate, and **heat under reflux:** (distill off product after the reaction has finished using distillation set up)



#### Observation

Orange dichromate solution changes to green colour of  $\text{Cr}^{3+}$  ions



Anti-bumping granules are added to the flask in both distillation and reflux to prevent vigorous, uneven boiling.

## Purifying an organic liquid

- Put the distillate of impure product into a separating funnel
- wash product by adding either
  - sodium hydrogencarbonate solution, shaking and releasing the pressure from  $\text{CO}_2$  produced.
  - Saturated sodium chloride solution
- Allow the layers to separate in the funnel, and then run and discard the aqueous layer.
- Run the organic layer into a clean, dry conical flask and add three spatula loads of drying agent (anhydrous sodium sulphate) to dry the organic liquid.
- Carefully decant the liquid into the distillation flask
- Distill to collect pure product

Sodium hydrogencarbonate will neutralise any remaining reactant acid.

Sodium chloride will help separate the organic layer from the aqueous layer

The drying agent should

- be insoluble in the organic liquid
- not react with the organic liquid

Separating funnel

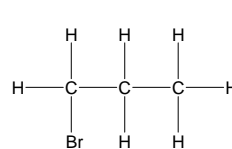


# Halogenoalkanes

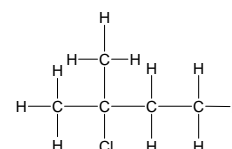
## Naming Halogenoalkanes

Based on original alkane, with a *prefix* indicating halogen atom:  
**Fluoro** for F; **Chloro** for Cl; **Bromo** for Br; **Iodo** for I.

Substituents are listed **alphabetically**



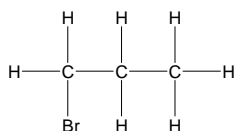
1-bromopropane



2-chloro-2-methylbutane

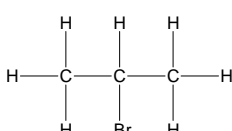
## Classifying Halogenoalkanes

Halogenoalkanes can be classified as primary, secondary or tertiary depending on the number of carbon atoms attached to the C-X functional group.



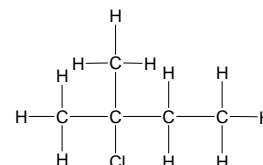
### Primary halogenoalkane

One carbon attached to the carbon atom adjoining the halogen



### Secondary halogenoalkane

Two carbons attached to the carbon atom adjoining the halogen



### Tertiary halogenoalkane

Three carbons attached to the carbon atom adjoining the halogen

## Reactions of Halogenoalkanes

Halogenoalkanes undergo either **substitution** or **elimination** reactions

### Nucleophilic substitution reactions

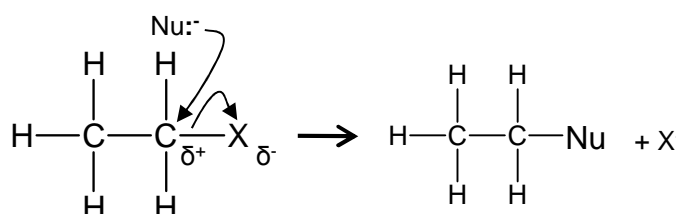
Substitution: swapping a halogen atom for another atom or groups of atoms

Nucleophile: electron pair donator e.g.  $\text{:OH}^-$ ,  $\text{:NH}_3$ ,  $\text{CN}^-$

**The Mechanism:** We draw (or **outline**) mechanisms to show in detail how a reaction proceeds

$\text{:Nu}$  represents any nucleophile – they always have a **lone pair** and act as **electron pair donors**

The nucleophiles attack the positive carbon atom



The carbon has a small positive charge because of the electronegativity difference between the carbon and the halogen



We use curly arrows in mechanisms (with two line heads) to show the movement of two electrons

A curly arrow will always **start** from a **lone pair** of electrons or the **centre of a bond**

**The rate of these substitution reactions depends on the strength of the C-X bond**

The weaker the bond, the easier it is to break and the faster the reaction.

The iodoalkanes are the fastest to substitute and the fluoroalkanes are the slowest. The strength of the C-F bond is such that fluoroalkanes are very unreactive

	Bond enthalpy / $\text{kJmol}^{-1}$
C-I	238
C-Br	276
C-Cl	338
C-F	484

## Comparing the rate of hydrolysis reactions

**Hydrolysis** is defined as the splitting of a molecule ( in this case a halogenoalkane) by a reaction with water



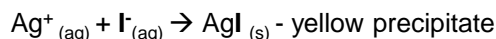
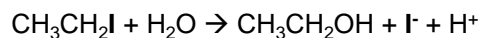
**Aqueous silver nitrate** is added to a halogenoalkane and the halide leaving group combines with a silver ion to form a **SILVER HALIDE PRECIPITATE**.

The precipitate only forms when the halide ion has left the halogenoalkane and so the rate of formation of the precipitate can be used to compare the reactivity of the different halogenoalkanes.

The **quicker** the **precipitate** is formed, the **faster** the **substitution** reaction and the **more reactive** the haloalkane

The rate of these substitution reactions depends on the strength of the C-X bond . The weaker the bond, the easier it is to break and the faster the reaction.

**Water** is a **poor nucleophile** but it can react **slowly** with halogenoalkanes in a substitution reaction



The iodoalkane forms a precipitate with the silver nitrate first as the C-I bond is weakest and so it hydrolyses the quickest

$\text{AgI}_{(\text{s})}$  - yellow precipitate  
 $\text{AgBr}_{(\text{s})}$  - cream precipitate  
 $\text{AgCl}_{(\text{s})}$  - white precipitate

↑ forms faster

## Nucleophilic substitution with aqueous hydroxide ions

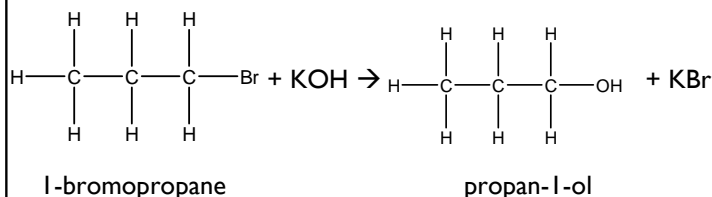
**Change in functional group:** halogenoalkane → alcohol

**Reagent:** potassium (or sodium) hydroxide

**Conditions:** In aqueous solution; Heat under reflux

**Mechanism:** Nucleophilic Substitution

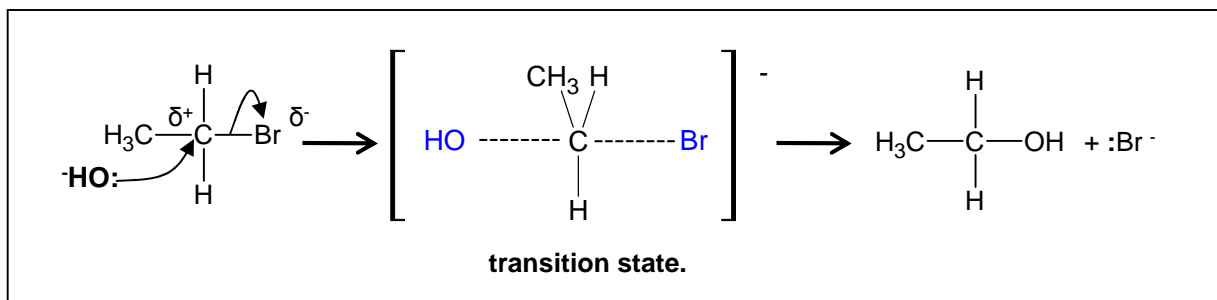
**Role of reagent:** Nucleophile,  $\text{OH}^-$



The  $\text{OH}^-$  is a stronger nucleophile than water as it has a full negative charge and so is more strongly attracted to the  $\text{C}^\delta+$

The **aqueous** conditions needed is an important point. If the solvent is changed to **ethanol** an elimination reaction occurs

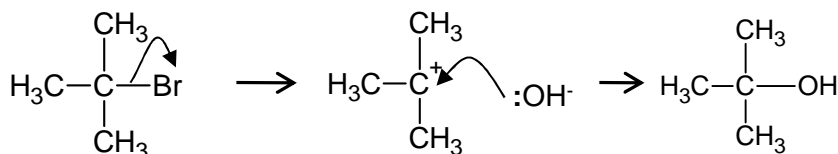
## $\text{S}_{\text{N}}2$ nucleophilic substitution mechanism for halogenoalkanes



This mechanism occurs with primary halogenoalkanes

## SN<sub>1</sub> nucleophilic substitution mechanism for tertiary halogenoalkanes

Tertiary haloalkanes undergo nucleophilic substitution in a different way



The Br first breaks away from the haloalkane to form a carbocation intermediate

The hydroxide nucleophile then attacks the positive carbon

Tertiary halogenoalkanes undergo this mechanism as the tertiary carbocation is made stabilised by the electron releasing methyl groups around it. (see alkenes topic for another example of this). Also the bulky methyl groups prevent the hydroxide ion from attacking the halogenoalkane in the same way as the mechanism above

Primary halogenoalkanes don't do the SN<sub>1</sub> mechanism because they would only form an unstable primary carbocation.

## Nucleophilic substitution with ammonia

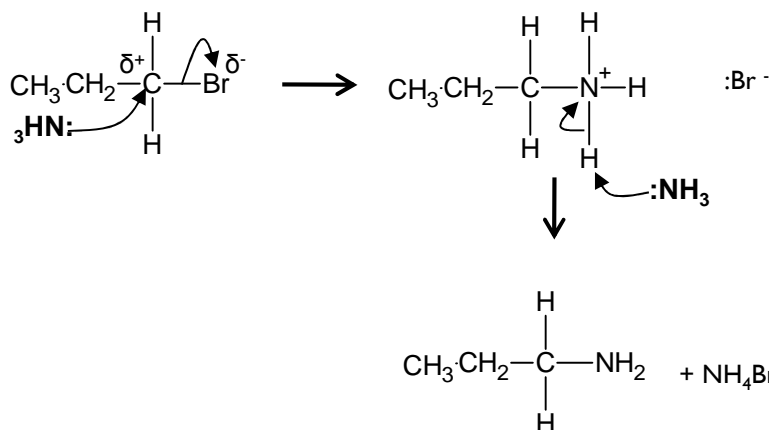
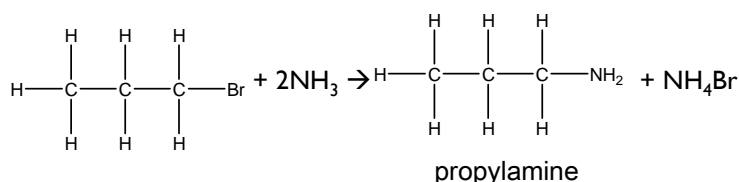
**Change in functional group:** halogenoalkane → amine

**Reagent:** NH<sub>3</sub> dissolved in ethanol

**Conditions:** Heating under pressure in a sealed tube

**Mechanism:** Nucleophilic Substitution

**Type of reagent:** Nucleophile, :NH<sub>3</sub>

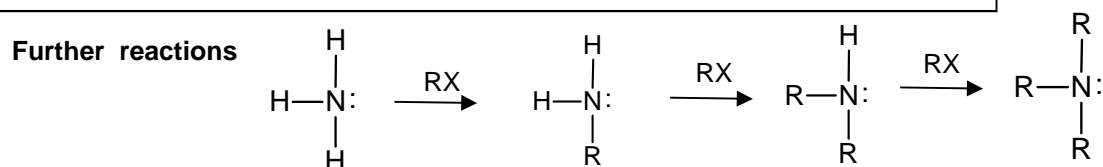


Naming amines:

In the above example propylamine, the propyl shows the 3 C's of the carbon chain.

Sometimes it is easier to use the IUPAC naming for amines e.g. Propan-1-amine

Further substitution reactions can occur between the haloalkane and the amines formed leading to a lower yield of the amine. Using excess ammonia helps minimise this.





## Elimination reaction of halogenoalkanes

Elimination: removal of small molecule (often water) from the organic molecule

### Elimination with alcoholic hydroxide ions

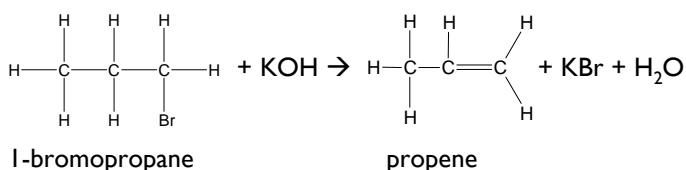
**Change in functional group:** halogenoalkane → alkene

**Reagents:** Potassium (or sodium) hydroxide

**Conditions:** In *ethanol*; Heat

**Mechanism:** Elimination

**Role of reagent:** Base, OH<sup>-</sup>



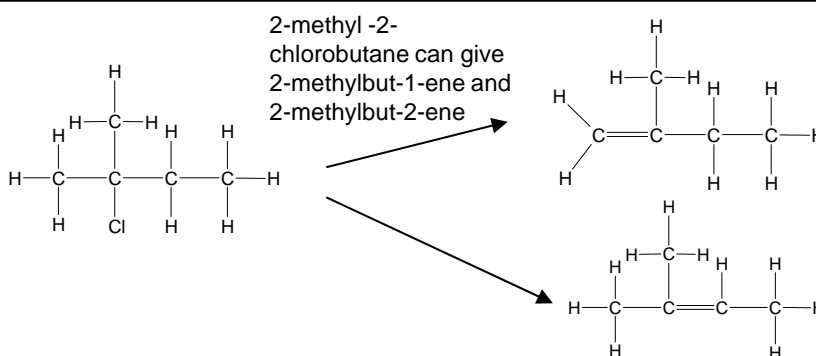
Note the importance of the solvent to the type of reaction here.

**Aqueous: substitution**

**Alcoholic: elimination**

Often a mixture of products from both elimination and substitution occurs

With unsymmetrical secondary and tertiary halogenoalkanes two (or sometimes three) different structural isomers can be formed



The structure of the halogenoalkane also has an effect on the degree to which substitution or elimination occurs in this reaction.

Primary tends towards substitution

Tertiary tends towards elimination

## Uses of halogenoalkanes

Haloalkanes have been used as **refrigerants**, **fire retardants**, pesticides and **aerosol propellants**

chloroalkanes and chlorofluoroalkanes can be used as solvents

CH<sub>2</sub>Cl<sub>2</sub> was used as the solvent in dry cleaning

Some halogenoalkanes have low flammability

Many of these uses have now been stopped due to the toxicity of halogenoalkanes and also their detrimental effect on the ozone layer