

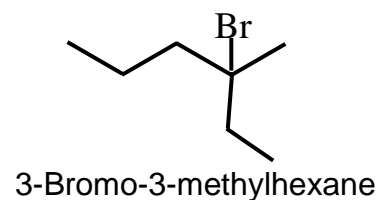
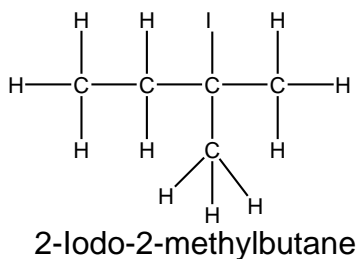
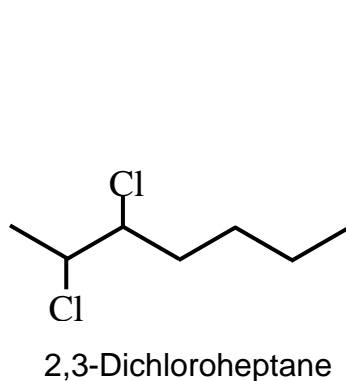
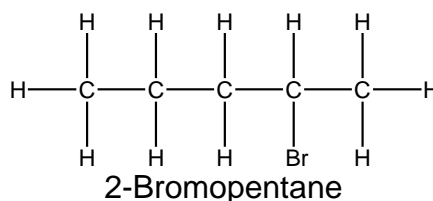
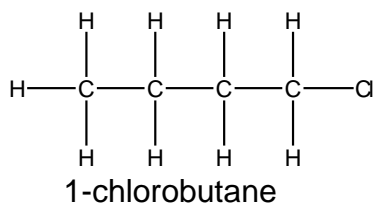
Halogenoalkanes and Alcohols

Halogenoalkanes

Halogenoalkanes contain a halogen as the functional group R-Hal.

The first part of the name of a halogenoalkane gives the position and name of the halogen concerned.

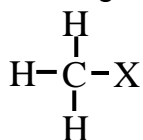
The second part of the name is based on the rest on the hydrocarbon structure.



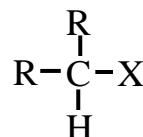
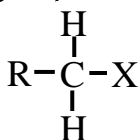
Types of Halogenoalkanes

There are three types of halogenoalkane; primary, secondary and tertiary.

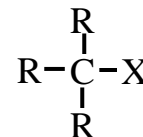
They are classified according to the number of carbon groups attached to the carbon with the halogen, X, group.



Primary



Secondary



Tertiary

No or one carbon (R) group attached to the carbon with the X group is a primary halogenoalkane.

Two carbon (R) groups attached to the carbon with the X group is a secondary halogenoalkane.

Three carbon (R) groups attached to the carbon with the X group is a tertiary halogenoalkane

Chemical properties of Halogenoalkanes

Fluoroalkanes are different from the other halogen derivatives, since the C–F bond is so strong that they are very unreactive. Most of the discussion here will refer to RCl, RBr and RI.

Chloromethane, bromomethane, and chloroethane are gases, while the rest are liquids which do not mix with water as they do not have the ability to hydrogen bond.

Preparation of Halogenoalkanes

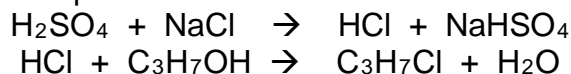
Halogenoalkanes are generally made by reacting the appropriate alcohol with a halogenating reagent.

Halogenating agents include phosphorus pentachloride, sodium chloride with concentrated sulphuric acid, sodium bromide with concentrated phosphoric acid and phosphorus with iodine.

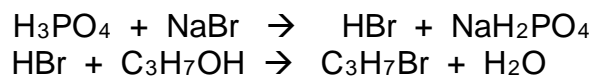
Phosphorus pentachloride reacts vigorously with alcohols at room temperature.



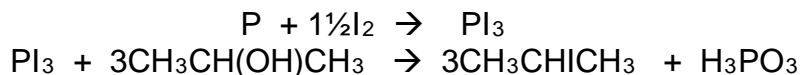
Chloro- compounds can also be formed by heating the alcohol under reflux with sodium chloride and concentrated sulphuric acid.



To form a bromo- compound, the alcohol is heated under reflux with sodium bromide and concentrated phosphoric acid. The concentrated phosphoric acid reacts with the sodium bromide to form hydrogen bromide, and the hydrogen bromide carries out the substitution.



To produce iodo- compounds, the alcohol is mixed with red phosphorus and iodine is added gradually. The mixture is then heated under reflux.



Concentrated sulphuric acid cannot be used to make bromoalkanes or iodoalkanes as the halide ion is oxidized to the halogen.

Reactions of Halogenoalkanes

Halogenoalkanes commonly undergo **nucleophilic substitution** and **elimination** reactions.

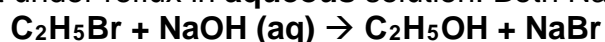
Nucleophilic substitution reactions

A **nucleophile** is a species (molecule or negative ion) which can donate an electron pair in a chemical reaction.

Halogenoalkanes undergo substitution reactions with nucleophiles such as OH⁻ and NH₃.

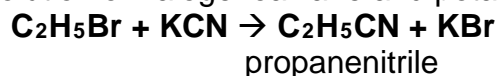
with potassium hydroxide.

Conditions: Heat under reflux in **aqueous** solution. Both NaOH or KOH are suitable.



with potassium cyanide

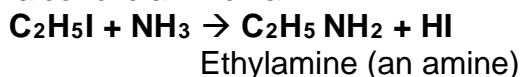
Conditions: Reflux solution of halogenoalkane and potassium cyanide in ethanol.



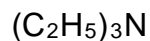
This adds a carbon atom to the chain and forms a nitrile.

with ammonia

Conditions: Heat with concentrated ammonia in a sealed tube.
or heat with alcoholic ammonia.



Other products include: (C₂H₅)₂NH and



Amines are molecules containing a N functional group.

Elimination reactions

If a halogenoalkane is boiled with potassium hydroxide solution in ethanol rather than water an elimination reaction takes place in which an alkene is formed and hydrogen halide is given off (eliminated).

Conditions: Heat under reflux with **alkali** and ethanol as solvent. Use KOH here.

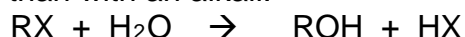


Identification of halogenoalkanes – Reaction with Silver nitrate solution.

In the presence of water, halogenoalkanes undergo **hydrolysis**.

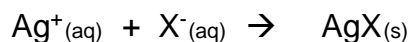
The halogenoalkanes have a slightly polarised C-Hal bond. Water acts as a nucleophile towards the carbon atom in this bond. As a result, the -OH group substitutes for the halogen, giving an alcohol and a hydrogen halide.

The reaction is much slower than with an alkali.



The hydrogen halide formed will dissolve in the water forming H^+ and X^- ions. The ions then react with the silver ions in the solution producing a precipitate.

The appearance of the precipitate depends upon the halide ion generated in the hydrolysis reaction.



This reaction is used to test for halogenoalkanes.

- Heat sample of halogenoalkane with aqueous hydroxide ions.
- Acidify with dilute aqueous nitric acid.
- Add a few drops of aqueous silver nitrate.
- A white precipitate soluble in dilute aqueous ammonia, indicates chloride.
- A buff precipitate insoluble in dilute aqueous ammonia but soluble in concentrated aqueous ammonia, indicates bromide.
- A yellow precipitate insoluble in concentrated aqueous ammonia indicates iodide.

Reactivity of halogenoalkanes

Results of investigations show that the rate of hydrolysis of the halogenoalkanes occurs in the order:



The ease of reaction depends on the ease of breaking the C-Hal bond:

Bond :	C-I	C-Br	C-Cl	C-F
Bond enthalpy terms (kJ mol^{-1}):	+238	+276	+338	+484

Thus the ease of bond breaking is, **C-I > C-Br > C-Cl > C-F**.

(This outweighs the effects caused by greater polarization in the C-Hal bond).

Uses of halogenoalkanes

Halogenoalkanes are used as fire retardants and refrigerants as they are unreactive and particularly for the fire retardants they are non-combustible.

Freon 12 CF_2Cl_2 is a refrigerant and an example of a chlorofluorocarbon (CFC). The C-F and C-Cl bonds are very strong. The result is that it does not decompose easily so lasts for the lifetime of a refrigerator. It does not decompose quickly when discarded but does so in the upper atmosphere. The radicals it forms react with ozone. The loss of ozone leads to an increase in UV radiation reaching the Earth's surface and a corresponding increase in skin cancers in humans.

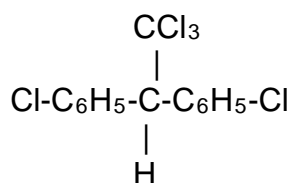
Modern refrigerants are hydrofluorocarbons, HFCs, such as $\text{CF}_3\text{CH}_2\text{F}$. They do not lead to ozone depletion.

PVC used as electrical insulator $-\text{[CH}_2\text{-CHCl-]}_n-$

The C-Cl bond is strong so PVC insulation lasts a long time but when discarded it does not rot (it is not biodegradable).

Teflon, or **poly(tetrafluoroethene)** is essentially poly(ethene) chains in which all the H atoms have been replaced by fluorines: $-\text{CF}_2-\text{CF}_2-\text{CF}_2-\text{CF}_2-\text{CF}_2-\text{CF}_2-\text{CF}_2-\text{CF}_2-$ etc. It is used to line **non-stick frying pans and saucepans**, and for low-friction bearings. As the C-F is very strong it is non-biodegradable.

DDT is a pesticide used to kill mosquitos.



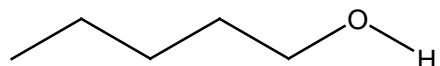
The strong C-Cl bonds give DDT a long life in the field killing pests. It is however so long lived that it persists in the environment and builds up in the food chain threatening creatures at the top of the chain.

Alcohols

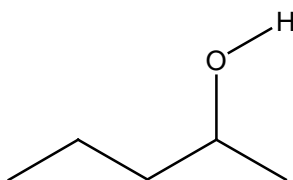
Alcohols contain the -OH functional group.

General formula – $C_nH_{2n+1}OH$

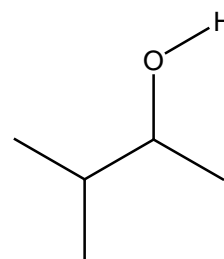
The first part of the name of an alcohol is according to the longest carbon atom sequence. The second part of the name is -ol. A number will be included to indicate the position of the alcohol group.



Pentanol or pentan-1-ol



Pentan-2-ol

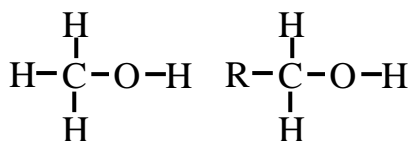


3-methylbutan-2-ol

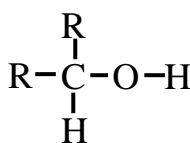
Types of Alcohol

There are three types of alcohol; primary, secondary and tertiary.

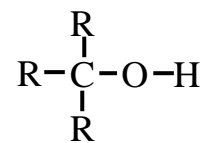
They are classified according to the number of carbon groups attached to the carbon with the OH group.



Primary



Secondary



Tertiary

No or one carbon (R) group attached to the carbon with the OH group is a primary alcohol.

Two carbon (R) groups attached to the carbon with the OH group is a secondary alcohol.

Three carbon (R) groups attached to the carbon with the OH group is a tertiary alcohol.

Physical properties of alcohols

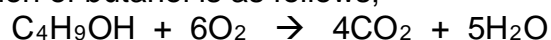
The OH group can take part in hydrogen-bonding, both as a donor (H is sufficiently $\delta+$) and as an acceptor (through the two lone pairs on the oxygen atom). As a result alcohols have higher melting and boiling points than hydrocarbons of comparable molar mass.

They are also more soluble in water because of H-bonding: ethanol is miscible with water in all proportions. As the non-polar hydrocarbon chain becomes longer, it becomes harder for water to dissolve the alcohol: from C₄ alcohols are less soluble, and don't mix with water.

Reactions of Alcohols

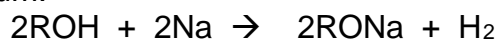
Combustion

All alcohols undergo combustion to form carbon dioxide and water. For example the equation for the combustion of butanol is as follows;



Reaction with sodium

All alcohols react with sodium.



This equation is similar to the reaction of sodium with water, except that an **alkoxide** is formed rather a hydroxide.

e.g. Ethanol and sodium $2\text{C}_2\text{H}_5\text{OH} + 2\text{Na} \rightarrow 2\text{C}_2\text{H}_5\text{ONa} + \text{H}_2$
Sodium ethoxide

Reaction with phosphorus pentachloride

All alcohols react with phosphorus pentachloride.

This is used as a test for the -OH group. The presence of the OH group can be shown by adding phosphorus pentachloride to the compound. A reaction takes place forming hydrogen chloride which appears as steamy white fumes.



In the reaction with phosphorus pentachloride a chloro group replaces the -OH group.

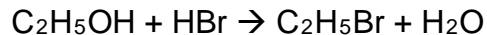
e.g. Propanol and phosphorus pentachloride



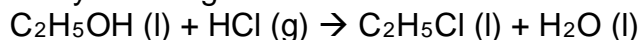
Reaction with other halogenating agents

Alkyl bromides can be made from the reaction of an alcohol with HBr.

HBr is made **in situ** from KBr and H₂SO₄ forms bromoalkanes during heating under reflux.



Alkyl chlorides can be made by refluxing the alcohol with conc. HCl in the presence of ZnCl₂



Iodoalkanes can be made in a reaction phosphorus triiodide from iodine and red phosphorus.



The relative reactivities of alcohols in halogenation are tertiary > secondary > primary alcohol.

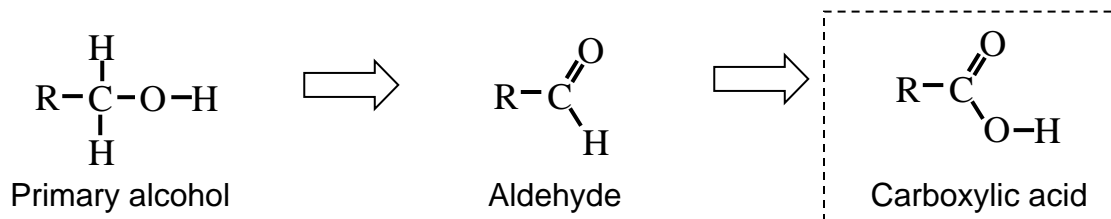
Oxidation of alcohols

Primary and secondary alcohols can be oxidised by heating with a mixture of dilute sulphuric acid with sodium or potassium dichromate(VII) solution.

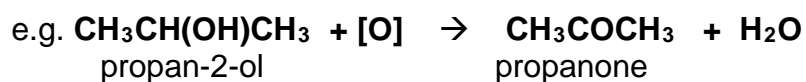
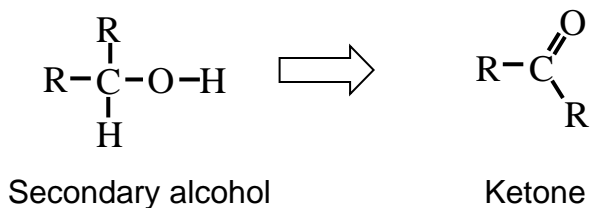
Acidified dichromate(VI) solution produces a colour change from **orange to blue-green** when it has undergone oxidation reactions.

In writing equations for these oxidation reactions [O] is used to represent the oxidising agent.

Primary alcohols form an aldehyde, and then on further oxidation, form carboxylic acids.



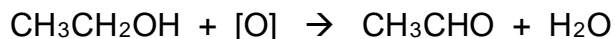
Secondary alcohols form ketones, but no further oxidation takes place.



Tertiary alcohols do not react with oxidizing agents.

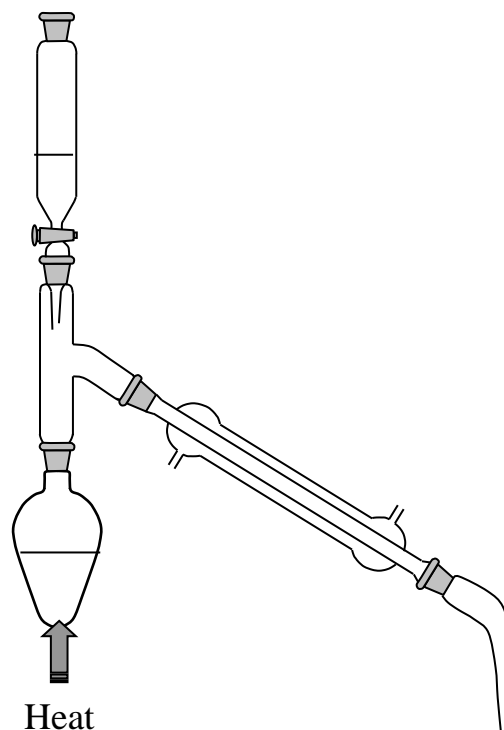
Partial Oxidation to aldehydes

e.g. ethanol to ethanal.



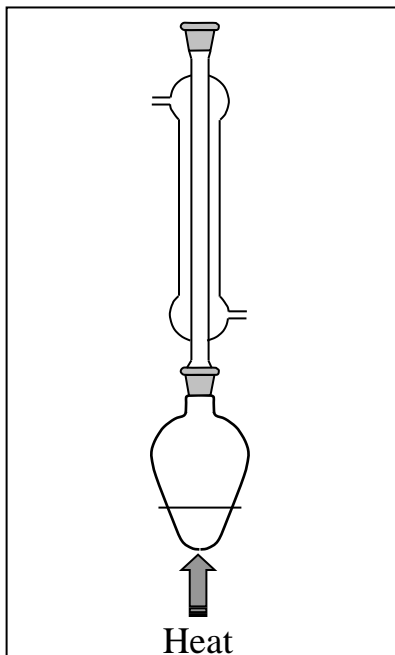
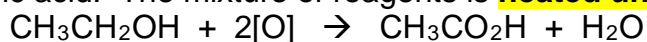
To make the aldehyde, the one reagent is added dropwise to the other and the product is distilled off as it forms.

By distilling the aldehyde off as it forms, it means it will not undergo further oxidation to the acid.



Total Oxidation to Carboxylic acids

e.g. ethanol to ethanoic acid. The mixture of reagents is heated under reflux.



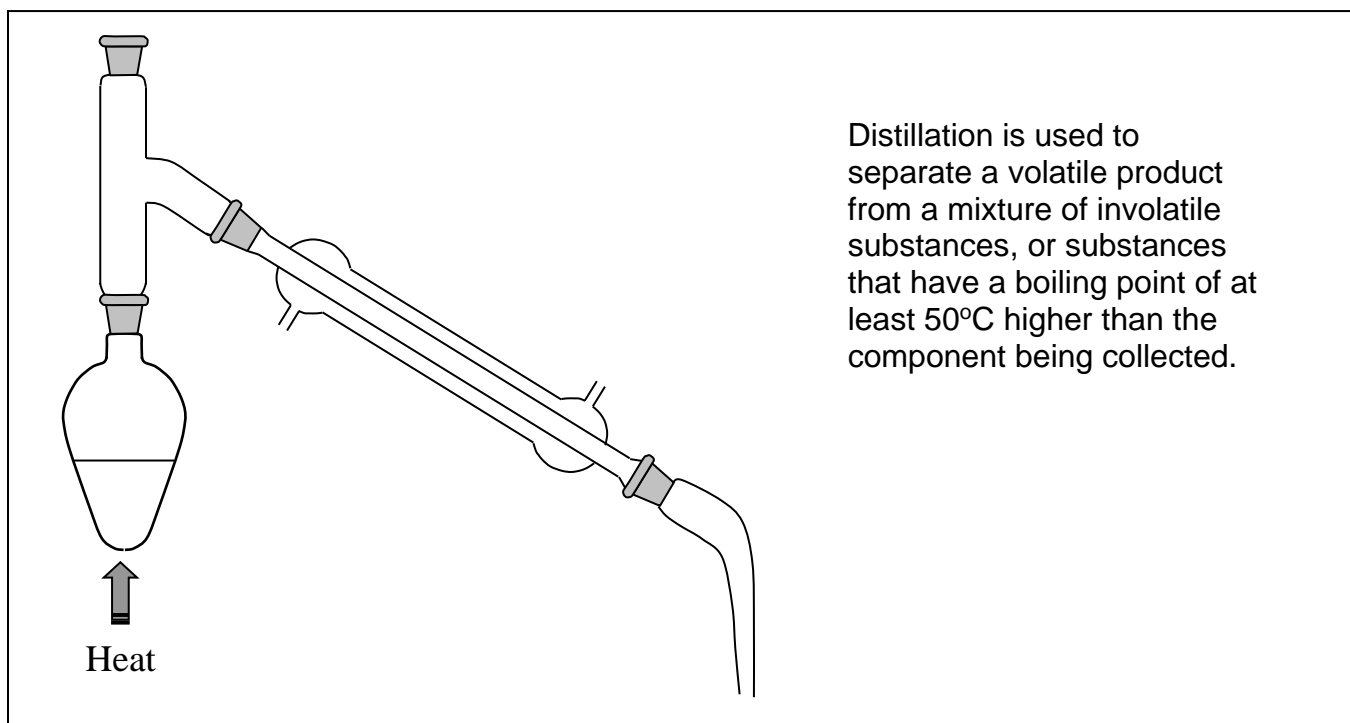
Heating under reflux

The apparatus shown here is used a large number of organic preparations.

The reaction mixture is placed in the pear shaped flask. It has a reflux condenser* fitted. This means that as the reactants are heated and the volatile liquids boil off, they are converted back to liquid in the condenser and return to the flask.

*A reflux condenser "is not a special type of condenser, it is an ordinary condenser fitted so that reflux takes place.

Once the carboxylic has been formed, it needs to be separated from the reaction mixture and other products. This is done by **distillation**.



Distillation is used to separate a volatile product from a mixture of involatile substances, or substances that have a boiling point of at least 50°C higher than the component being collected.