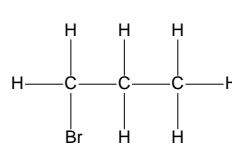


16 Halogenoalkanes

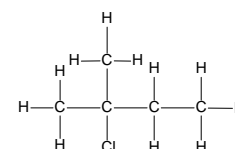
Naming Halogenoalkanes

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**



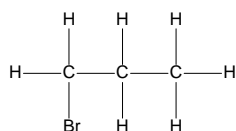
1-bromopropane



2-chloro-2-methylbutane

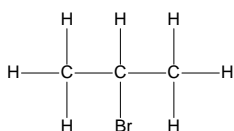
Classifying halogenoalkanes

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



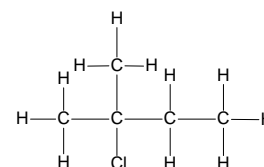
Primary halogenoalkane

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

Organic reactions are classified by their mechanisms

1. Nucleophilic substitution reactions

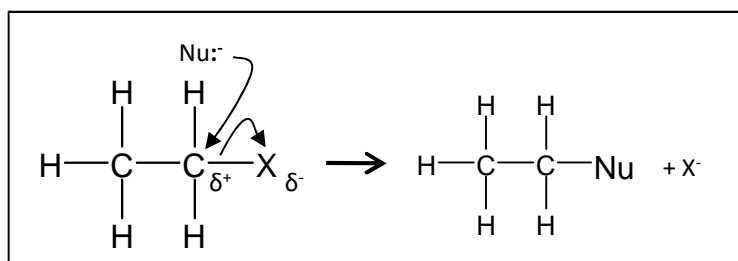
Substitution: swapping a halogen atom for another atom or groups of atoms

Nucleophile: electron pair donor e.g. :OH^- , :NH_3 , CN^-

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

: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 / 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 haloalkane) by a reaction with water



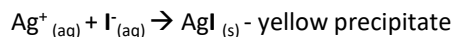
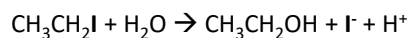
Aqueous silver nitrate is added to a haloalkane and the halide leaving group combines with a silver ion to form a **SILVER HALIDE PRECIPITATE**.

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

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 haloalkanes 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

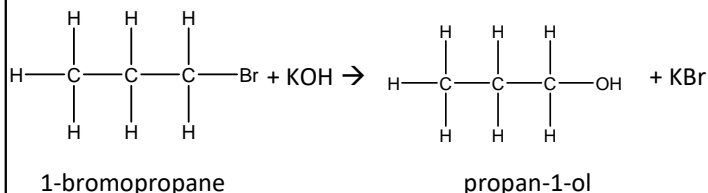
Change in functional group: halogenoalkane → alcohol

Reagent: potassium (or sodium) hydroxide

Conditions: In aqueous solution; Heat under reflux

Mechanism: Nucleophilic Substitution

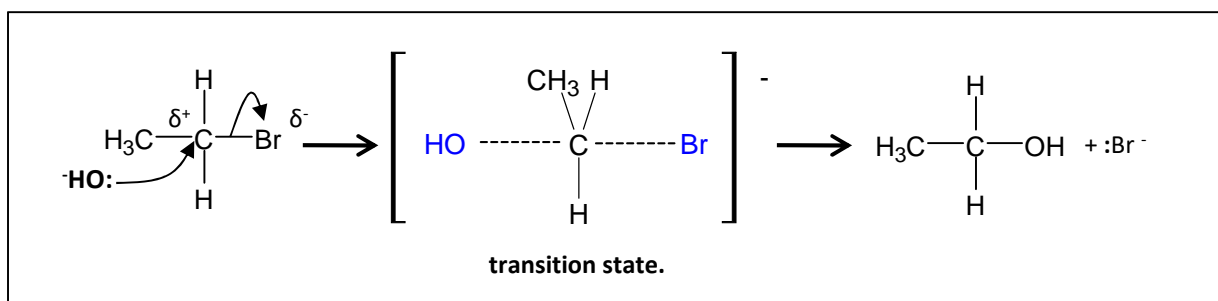
Role of reagent: Nucleophile, OH^-



The 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

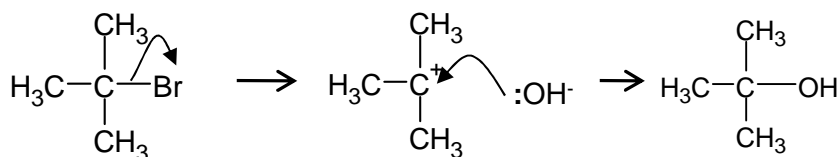
$\text{S}_{\text{N}}2$ nucleophilic substitution mechanism for halogenoalkanes



This mechanism occurs with primary halogenoalkanes

SN₁ 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 SN₁ mechanism because they would only form an unstable primary carbocation.

Nucleophilic substitution with ammonia

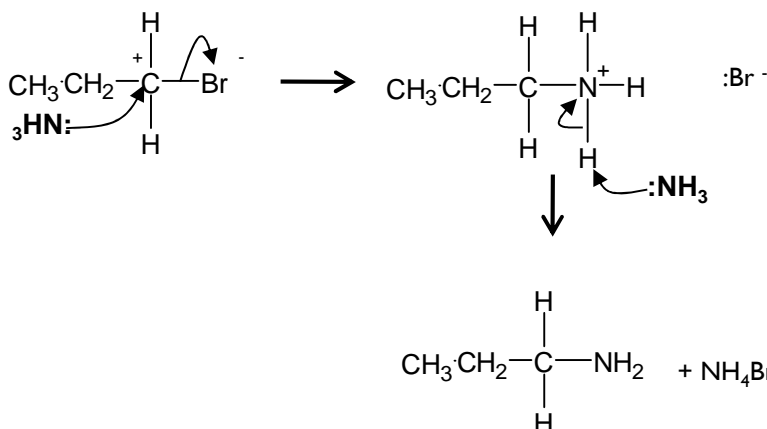
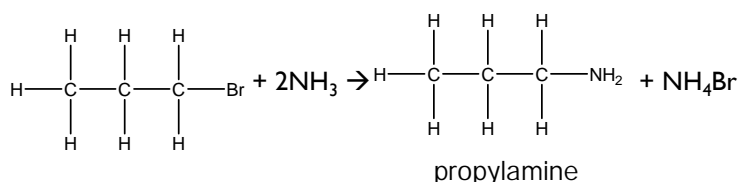
Change in functional group: halogenoalkane → amine

Reagent: NH₃ dissolved in ethanol

Conditions: Heating under pressure in a sealed tube

Mechanism: Nucleophilic Substitution

Type of reagent: Nucleophile, :NH₃



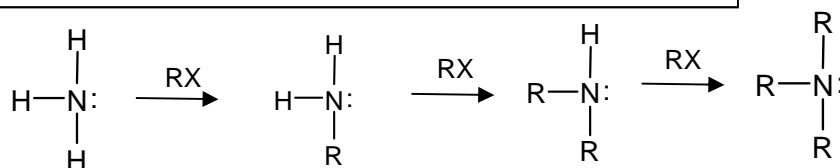
Naming amines:

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.

Further reactions



Nucleophilic substitution with cyanide ions

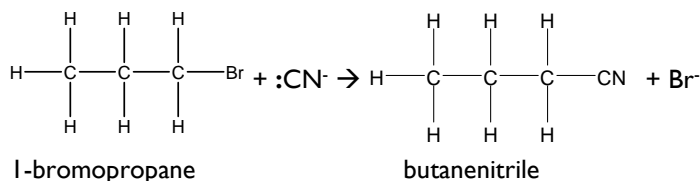
Change in functional group: halogenoalkane → nitrile

Reagent: KCN dissolved in ethanol/water mixture

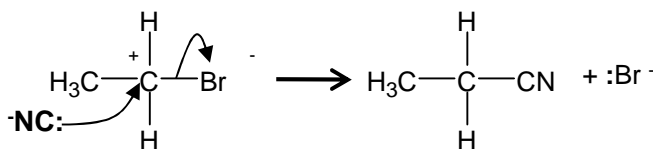
Conditions: Heating under reflux

Mechanism: Nucleophilic Substitution

Type of reagent: Nucleophile, :CN⁻



Note: the mechanism is identical to the above one



This reaction increases the length of the carbon chain (which is reflected in the name) In the above example butanenitrile includes the C in the nitrile group

Naming Nitriles

Nitrile groups have to be at the end of a chain. Start numbering the chain from the C in the CN

CH₃CH₂CN : propanenitrile

$\text{H}_3\text{C}-\underset{\text{CH}_3}{\text{CH}}-\text{CH}_2-\text{C}\equiv\text{N}$ 3-methylbutanenitrile

Note the naming: **butanenitrile** and not butannitrile.

Elimination reaction of halogenoalkanes

Elimination with alcoholic hydroxide ions

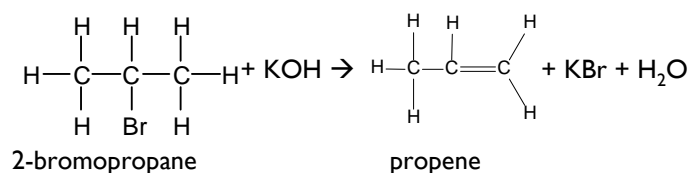
Change in functional group: halogenoalkane → alkene

Reagents: Potassium (or sodium) hydroxide

Conditions: In ethanol; Heat

Mechanism: Elimination

Type of reagent: Base, OH⁻



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

Uses of Halogenoalkanes

chloroalkanes and chlorofluoroalkanes can be used as solvents

CH_2Cl_2 was used as the solvent in dry cleaning

Halogenoalkanes have also been used as refrigerants, pesticides and aerosol propellants

Many of these uses depended on the unreactivity of Fluorine containing compounds. They often had low flammability

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

Ozone Chemistry

The naturally occurring ozone (O_3) layer in the upper atmosphere is beneficial as it filters out much of the sun's harmful UV radiation

Ozone in the lower atmosphere is a pollutant and contributes towards the formation of smog

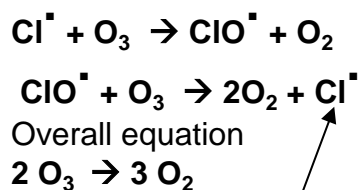
Man-made chlorofluorocarbons (CFC's) caused a hole to form in the ozone layer.

Chlorine atoms are formed in the upper atmosphere when energy from ultra-violet radiation causes C-Cl bonds in chlorofluorocarbons (CFCs) to break



The chlorine free radical atoms **catylse** the decomposition of ozone due to these reactions because they are regenerated. (They provide an alternative route with a lower activation energy)

They contributed to the formation of a hole in the ozone layer.



The regenerated Cl radical means that one Cl radical could destroy many thousands of ozone molecules

Legislation to ban the use of CFCs was supported by chemists and that they have now developed alternative chlorine-free compounds

HFCs (Hydro fluoro carbons) e.g.. CH_2FCF_3 are now used for refrigerators and air-conditioners. These are safer as they do not contain the C-Cl bond

The C-F bond is stronger than the C-Cl bond and is not affected by UV