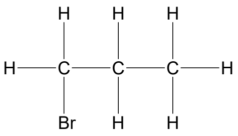
3.3 Halogenoalkanes

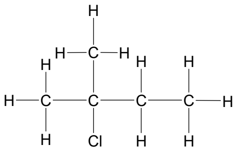
Naming Halogenoalkanes

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**



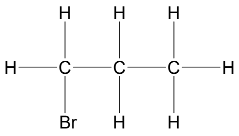
1-bromopropane



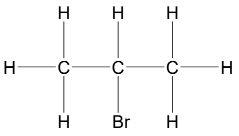
2-chloro-2-methylbutane

Classifying halogenoalkanes

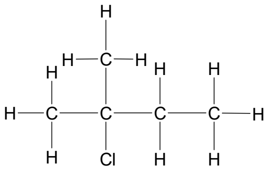
Halogenoalkanes can be classified as primary, secondary or tertiary depending on the number of carbon atoms attached to the C-X functional group.



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

Organic reactions are classified by their mechanisms

1. Nucleophilic substitution reactions

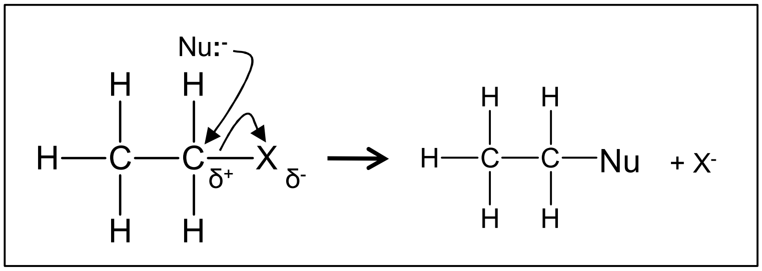
Substitution: swapping a halogen atom for another atom or groups of atoms

Nucleophile: electron pair donator 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 donators**

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.

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

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

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

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

$$CH_3CH_2X + H_2O \rightarrow CH_3CH_2OH + X^- + H^+$$

Aqueous silver nitrate is added to a halogenoalkane. 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.

$$CH_3CH_2I + H_2O \rightarrow CH_3CH_2OH + I^- + H^+$$

$Ag^+_{(aq)} + I^-_{(aq)} \rightarrow AgI_{(s)}$ - yellow precipitate

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

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

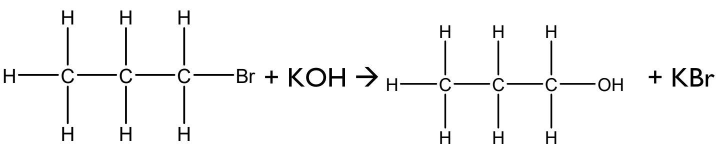
The rate of these substitution reactions depends on the strength of the C-X bond . The weaker the bond, the easier it is to break and the faster the reaction.

$AgI_{(s)}$ - yellow precipitate
$AgBr_{(s)}$ – cream precipitate
$AgCl_{(s)}$ – white precipitate

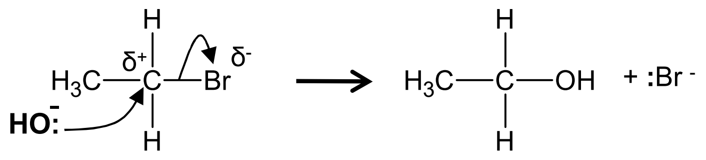
↑ forms faster

Nucleophilic substitution with *aqueous* hydroxide ions

Change in functional group*:* halogenoalkane → alcohol
Reagent: potassium (or sodium) hydroxide
Conditions: In ***aqueous solution***; warm
Mechanism: Nucleophilic substitution
Type of reagent: Nucleophile, OH^-



1-bromopropane   propan-1-ol

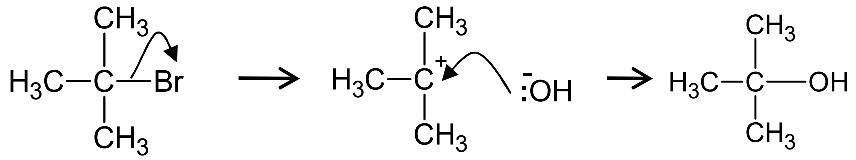


The **aqueous** conditions needed is an important point. If the solvent is changed to **ethanol** an elimination reaction occurs.

Alternative mechanism for tertiary halogenoalkanes

You don't need to learn this but there have been application of understanding questions on this

Tertiary halogenoalkanes undergo nucleophilic substitution in a different way



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

The hydroxide nucleophile then attacks the positive carbon

Tertiary halogenoalkanes undergo this mechanism as the tertiary carbocation is 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.

Nucleophilic substitution with cyanide ions

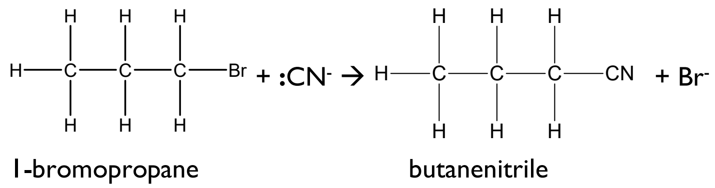
Change in functional group: halogenoalkane → nitrile

Reagent: KCN dissolved in **ethanol/water mixture**

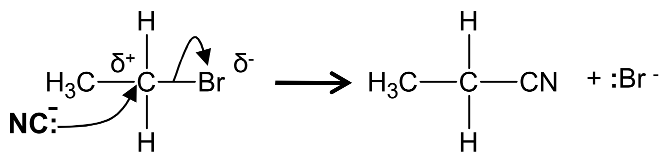
Conditions: Heating under reflux

Mechanism: Nucleophilic substitution

Type of reagent: Nucleophile, :CN^-



Note: the mechanism is identical to the above one

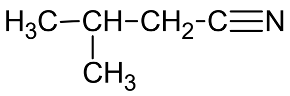


This reaction increases the length of the carbon chain (which is reflected in the name) In the above example butanenitrile includes the C in the nitrile group

Naming nitriles

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

CH_3CH_2CN : propanenitrile



$H_3C-\underset{\underset{CH_3}{|}}{CH}-CH_2-C\equiv N$ 3-methylbutanenitrile

Note the naming: but**ane**nitrile and not butannitrile.

Nucleophilic substitution with ammonia

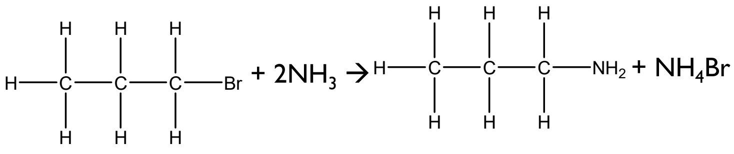
Change in functional group: **halogenoalkane → amine**

Reagent: NH_3 dissolved in ethanol

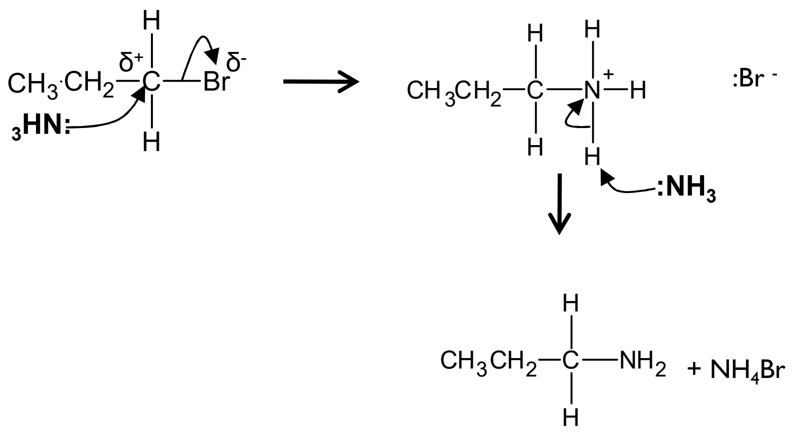
Conditions: Heating under pressure (in a sealed tube)

Mechanism: Nucleophilic substitution

Type of reagent: Nucleophile, :NH_3



propylamine



Naming amines:

In the above example prop**yl**amine, the propyl shows the 3 C's of the carbon chain.

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

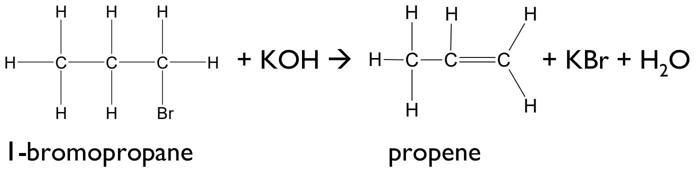
Further substitution reactions can occur between the halogenoalkane and the amines formed leading to a lower yield of the amine. Using excess ammonia helps minimise this.

2. Elimination reaction of halogenoalkanes

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

Elimination with alcoholic hydroxide ions

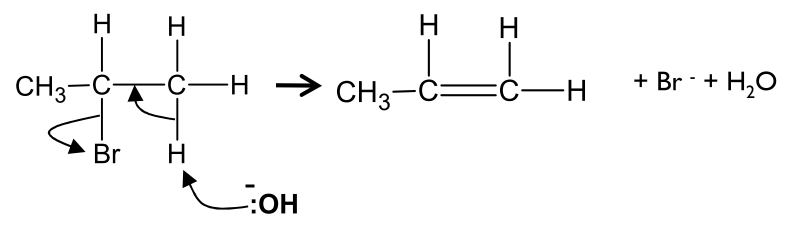
Change in functional group: halogenoalkane → alkene
Reagents: Potassium (or sodium) hydroxide
Conditions: In **ethanol** ; heat under reflux
Mechanism: Elimination
Type of reagent: Base, OH^-



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

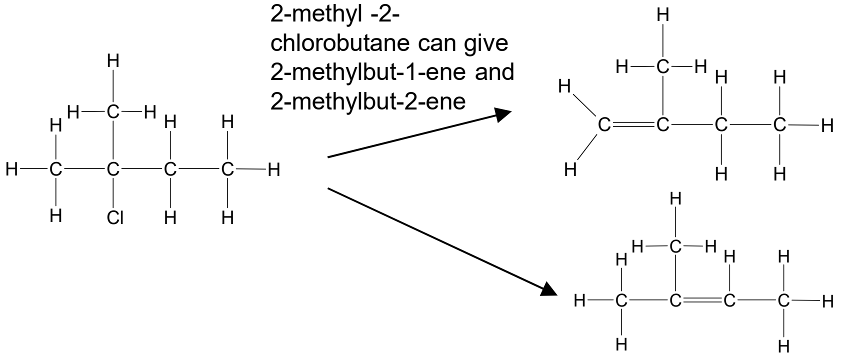
Aqueous: substitution

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



2-methyl -2-chlorobutane can give 2-methylbut-1-ene and 2-methylbut-2-ene

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

Chloroalkanes and chlorofluoroalkanes can be used as solvents.

CH_3CCl_3 was used as the solvent in dry cleaning.

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

Many of these uses have now been stopped due to the toxicity of halogenoalkanes 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 radicals are formed in the upper atmosphere when energy from ultra-violet radiation causes C–Cl bonds in chlorofluorocarbons (CFCs) to break.

$$CF_2Cl_2 \rightarrow CF_2Cl^{\bullet} + Cl^{\bullet}$$

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

These reactions contributed to the formation of a hole in the ozone layer.

$$Cl^{\bullet} + O_3 \rightarrow ClO^{\bullet} + O_2$$

$$ClO^{\bullet} + O_3 \rightarrow 2O_2 + Cl^{\bullet}$$

Overall equation

$$2\,O_3 \rightarrow 3\,O_2$$

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.