

8. The Haloalkanes

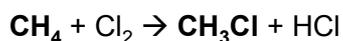
Synthesis of chloroalkanes

Reaction of alkanes with bromine / chlorine in UV light

In the presence of **UV light** alkanes react with chlorine to form a mixture of products with the halogens substituting hydrogen atoms.

In general, alkanes do not react with many reagents. This is because the C-C bond and the C-H bond are relatively strong

Overall Reaction



methane chloromethane

This is the overall reaction, but a more complex mixture of products is actually formed

To understand this reaction fully we must look in detail at how it proceeds step by step. This is called its **mechanism**

The **MECHANISM** for this reaction is called a **FREE RADICAL SUBSTITUTION**

It proceeds via a series of steps:
STEP ONE: **Initiation**
STEP TWO: **Propagation**
STEP THREE: **Termination**

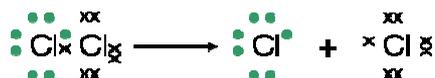
STEP ONE Initiation

Essential condition: UV light



The UV light supplies the energy to break the Cl-Cl bond. It is broken in preference to the others as it is the weakest.

The bond has broken in a process called **homolytic fission**.



each atom gets one electron from the covalent bond

When a bond breaks by homolytic fission it forms **Free Radicals**.

Free Radicals do not have a charge and are represented by a ●

DEFINITION

A **Free Radical** is a reactive species which possess an **unpaired electron**

STEP TWO Propagation



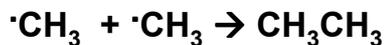
The chlorine free radicals are very reactive and remove an H from the methane leaving a methyl free radical

The methyl free radical reacts with a Cl₂ molecule to produce the main product and another Cl free radical

All propagation steps have a **free radical** in the **reactants** and in the **products**.

As the Cl free radical is regenerated, it can react with several more alkane molecules in a **CHAIN REACTION**

STEP THREE Termination



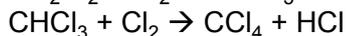
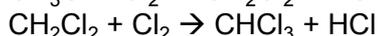
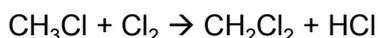
Collision of two free radicals *does not generate* further free radicals: the chain is **TERMINATED**.

Minor step leading to impurities of ethane in product

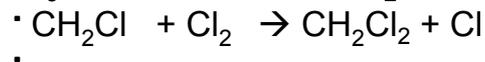
Further substitution

Excess Cl_2 present will promote further substitution and could produce CH_2Cl_2 , CHCl_3 and CCl_4

These reactions could occur



Example propagation steps that would lead to further substitution



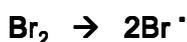
Applying the mechanism to other alkanes

The same mechanism is used: Learn the patterns in the mechanism

Example: Write mechanism of Br_2 and Propane

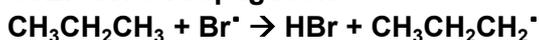
STEP ONE Initiation

Essential condition: UV light

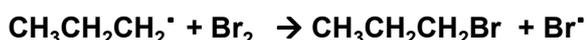


Br_2 splits in the same way as Cl_2

STEP TWO Propagation

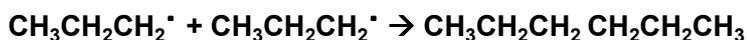
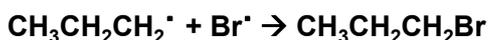


← Remove one H from the alkane to produce a radical



← To the radical produced in the previous step add a Br

STEP THREE Termination



Uses of haloalkanes

chloroalkanes and chlorofluoroalkanes can be used as solvents

CH_2Cl_2 was used as the solvent in dry cleaning

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

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

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

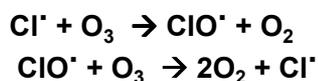
Ozone in the lower atmosphere is a pollutant and contributes towards the formation of smog

Man-made CFC's caused a hole to form in the ozone later.

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



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

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

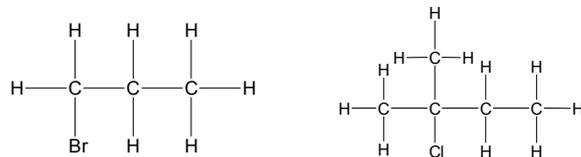
HFCs (Hydro fluoro carbons)
e.g. CH_2FCF_3 are now used for refrigerators and air-conditioners

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

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

Naming Haloalkanes

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



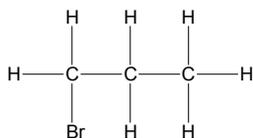
1-bromopropane

2-chloro-2-methylbutane

Substituents are listed **alphabetically**

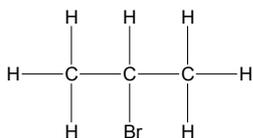
Classifying haloalkanes

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



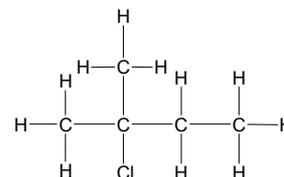
PRIMARY HALOALKANE

One carbon attached to the carbon atom adjoining the halogen



SECONDARY HALOALKANE

Two carbons attached to the carbon atom adjoining the halogen



TERTIARY HALOALKANE

Three carbons attached to the carbon atom adjoining the halogen

Reactions of Haloalkanes

Haloalkanes undergo either **substitution** or **elimination** reactions

Organic reactions are classified by their mechanisms

1. Nucleophilic substitution reactions

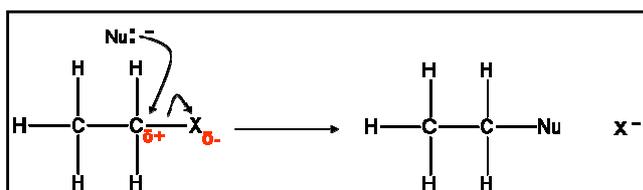
Substitution: swapping a halogen atom for another atom or groups of atoms

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

Nucleophilic substitution with aqueous hydroxide ions

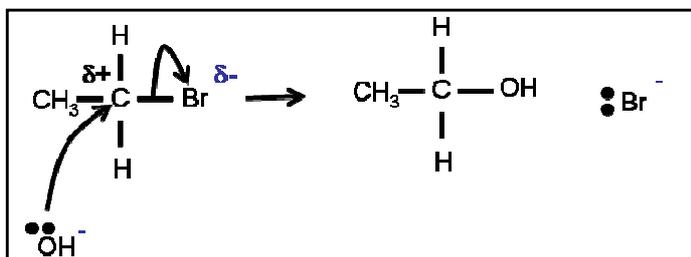
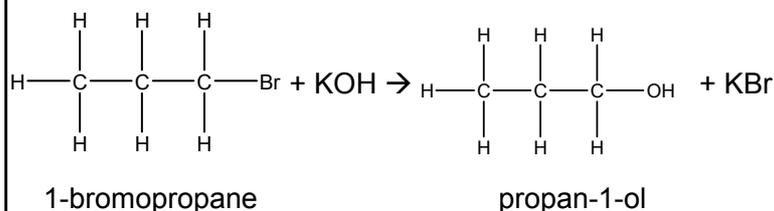
Change in functional group: haloalkane → alcohol

Reagent: potassium (or sodium) hydroxide

Conditions: In aqueous solution; Heat under reflux

Mechanism: Nucleophilic Substitution

Type of reagent: Nucleophile, OH⁻



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

Nucleophilic substitution with cyanide ions

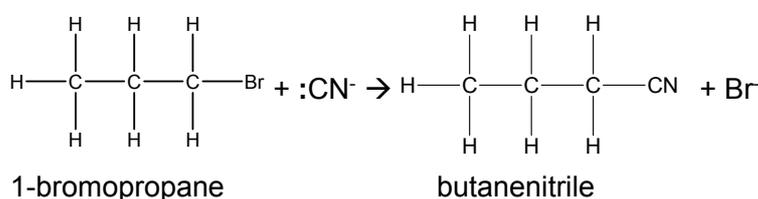
Change in functional group: haloalkane → nitrile

Reagent: KCN dissolved in ethanol

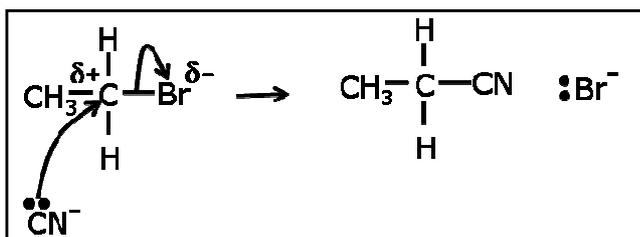
Conditions: Heating under reflux

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

Note the naming: butanenitrile and not butannitrile.

Nucleophilic substitution with ammonia

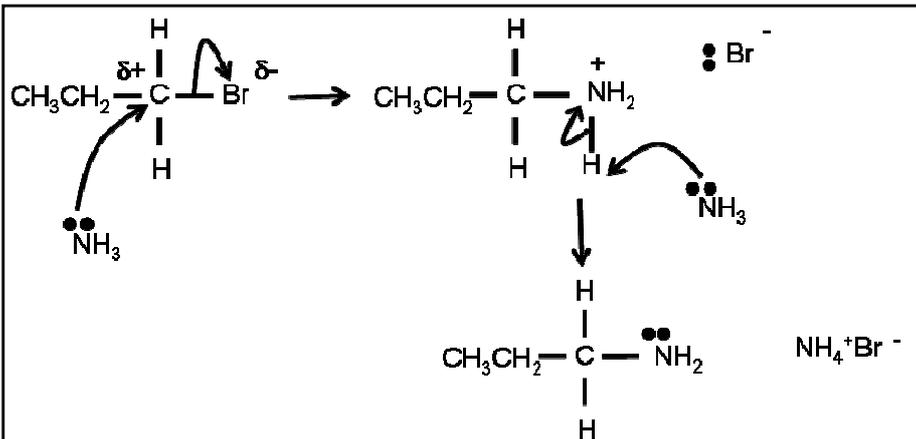
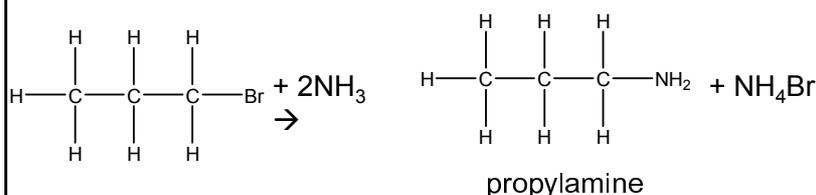
Change in functional group: haloalkane → amine

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 amino prefix to name amines e.g. **1-aminopropane**

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

