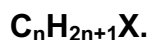

3.3 The Halogenoalkanes

Introduction:

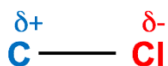
General formula



Where X is a halogen

- In the past they have been used as refrigerants and propellants in aerosols.
- They are no longer used in these due to their environmental impact on the ozone layer.

Reactivity

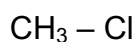


The more electronegative halogen produces a polar bond

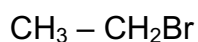
This makes the halogenoalkanes more reactive

Naming the halogenoalkanes

- The prefix **fluoro-**, **chloro-**, **bromo-** and **iodo-** are used:-



Chloromethane

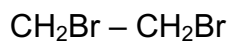


Bromoethane

- Isomers can be derived from a monosubstituted propane:-



- Multi halogen substituted compounds use **di**, **tri** to indicate how many of that halogen is present in the compound:-



1,2 - dibromoethane

Naming halogenoalkanes

Give the IUPAC name of the following halogenoalkanes:

Halogenoalkane	IUPAC name
$\text{CH}_3\text{CH}_2\text{Cl}$	
$\text{CH}_3\text{CHBrCH}_2\text{CH}_3$	
$\text{CH}_3\text{CH}_2\text{CHClCH}_2\text{CHBrCH}_3$	

Draw the structure of the following halogenoalkanes:

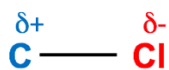
Halogenoalkane	Structural formula	Skeletal formula
2-bromo propane		
2,3-dichloro butane		
2-bromo 3-iodo hexane		

Complete the table below for 2-chloro pentane

Structural formula	Position Isomer	Chain Isomer

Reactions of the halogenoalkanes:

Reactivity



The polar bond makes the halogenoalkanes more reactive.

The C is deficient of electrons, $\delta+$

Nucleophiles



These have a pair of electrons to donate forming a dative covalent bond

Nucleophile: Donates a pair of electrons forming a dative covalent bond

Common Nucleophiles:

Cyanide



Ammonia



Hydroxide

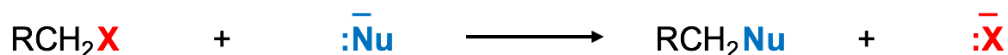


- Halogenoalkanes react in one of 2 ways:

- 1) Nucleophilic substitution
- 2) Elimination

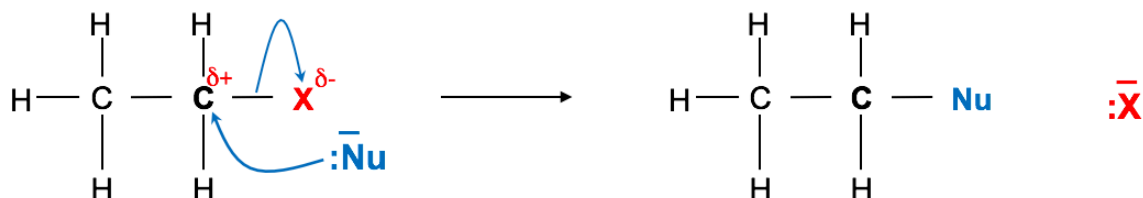
1) Nucleophilic substitution

Substitution: When one atom or group of atoms are swapped with another atom or group of atoms



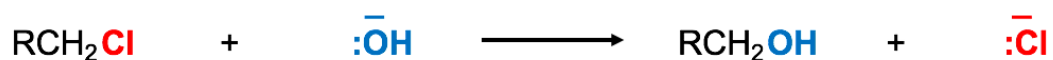
The mechanism:

X is a halogen



a) With aqueous hydroxide, OH⁻ Hydrolysis – forming alcohols

- This reaction converts a halogenoalkane to an alcohol

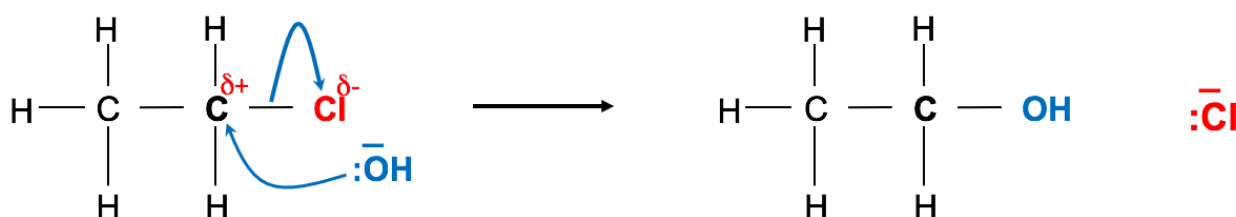


Reagents: Aqueous sodium hydroxide

Conditions: Reflux

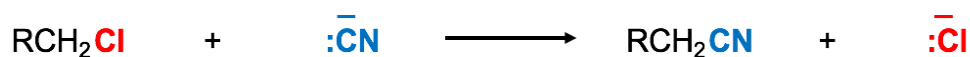
Hydrolysis: *Splitting a molecule apart by using water molecules*

The mechanism:



b) With ethanolic potassium cyanide, KCN – forming nitriles

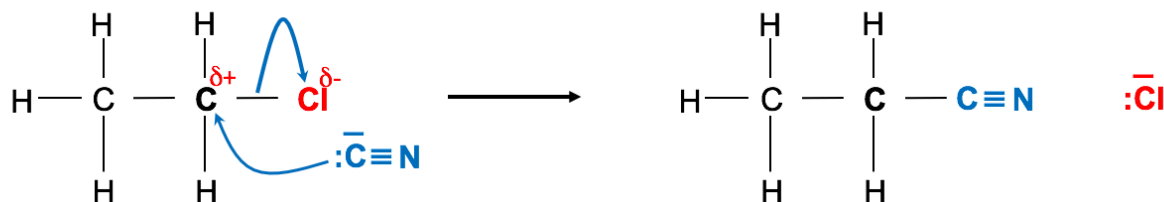
- This reaction converts a halogenoalkane to an alkyl nitrile
- This is a key reaction in chemical synthesis as the carbon chain length is increased



Reagents: Potassium cyanide dissolved in ethanol

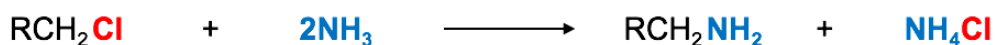
Conditions: Reflux

The mechanism:



c) With excess ethanolic ammonia, NH_3 – forming amines

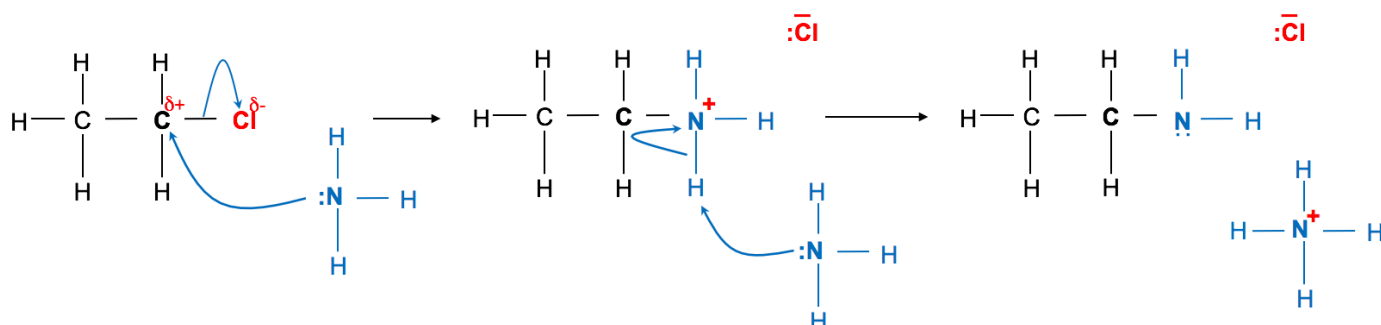
- This reaction converts a halogenoalkane to amines



Reagents: Excess ethanolic ammonia

Conditions: Reflux

The Mechanism

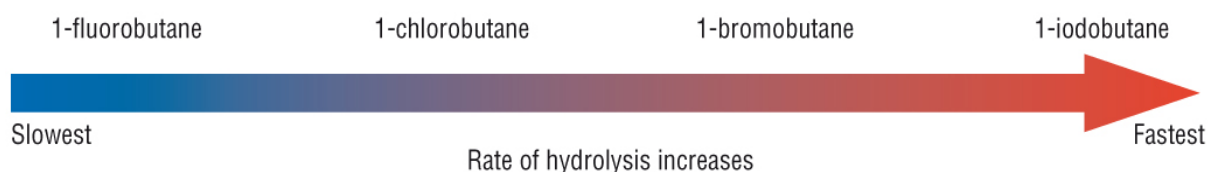


Rate of hydrolysis of the halogenoalkanes:

- The bond energies give us a good indication of the reactivity of the halogenoalkanes:
- The weakest would be expected to break first as it will have the **lowest activation energy**

bond	Enthalpy / kJ mol^{-1}
C-F	+467
C-Cl	+340
C-Br	+280
C-I	+240

- The rate can be measured by its reaction with a mixture of ethanol and **aqueous AgNO_3**
- Ethanol is the solvent
- The **water / aqueous hydrolyses** the halogenoalkane. In doing so, a **halide, X^-** is released.
- The **Ag^+** ions then form a **precipitate, AgX**
- The one that breaks first will form a precipitate with Ag^+ first:
- The **C - I** bond is the weakest of the 3 halogenoalkanes.
- This means that the bond would break more readily.
- This means that it would give the fastest reaction.
- In hydrolysis, bond enthalpy is more important than polarity:



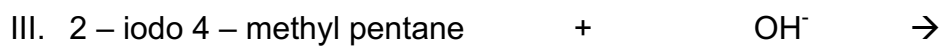
Questions:

a) All halogenoalkanes are liquids whereas the first 4 alkanes are gases. Use intermolecular forces to explain this?

b) Explain why are the halogenoalkanes more reactive than the alkenes?

c) Define the term **nucleophilic substitution**:

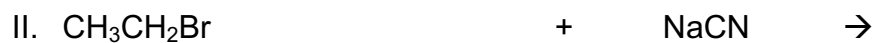
d) Complete the following hydrolysis reactions:



IV. Define hydrolysis

V. Draw the mechanism for d(II) include any dipole in your answer

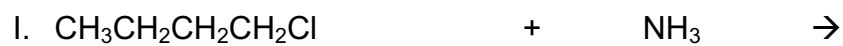
e) Complete the following reactions:



IV. Explain why are the above reactions so important in organic synthesis reactions?

V. Draw the mechanism for d(II) include any dipole in your answer

f) Complete the following reactions:

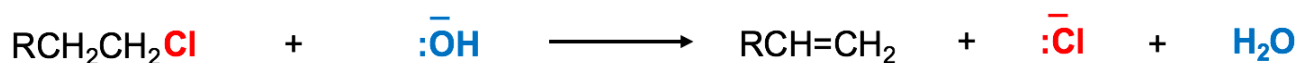


IV. Draw the mechanism for d(II) include any dipole in your answer

2) Elimination reactions

Elimination: Where a molecule loses atoms or groups of atoms

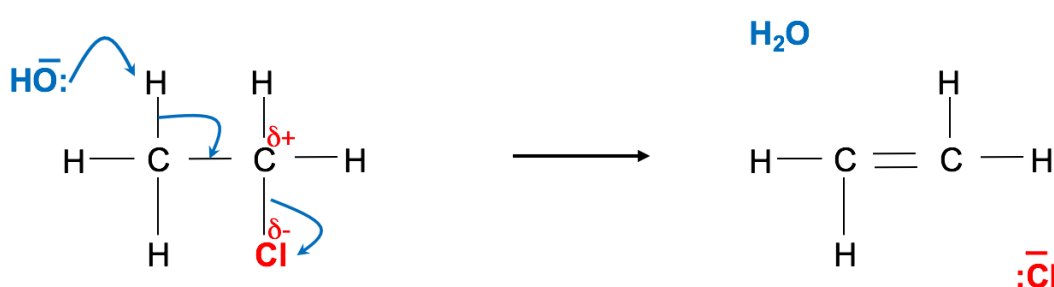
With ethanolic potassium hydroxide, reflux – forming alkenes



Reagents: KOH dissolved in ethanol

Conditions: Reflux

The mechanism:



- The **halogen** is always removed
- A **hydrogen on the adjacent carbon** is always removed (forming water with hydroxide)
- **C=C** is always formed between these 2 carbons

Substitution vs elimination

Substitution	Elimination
Aqueous conditions – substitution predominates	Ethanolic conditions – Elimination predominates
OH ⁻ behaves as a nucleophile	OH ⁻ behaves as a base (accepting a proton)
50 : 50 mixture of water : ethanol means substitution : elimination equally likely	

Questions:

a) Define the term **elimination**:

b) Complete the following elimination reactions:



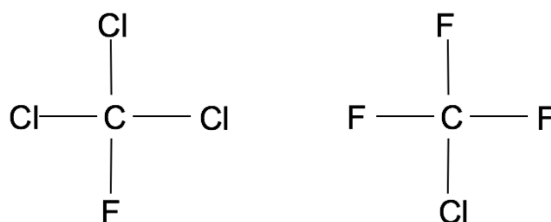
Tip: 2 organic products are formed here

IV. Draw the mechanism for b(II) include any dipoles in your answer

V. Explain why 2 products are formed in a(III) you may wish to use a mechanism to explain your answer

Halogenoalkanes and the environment:

Chlorofluorocarbons, CFC's:



Background:

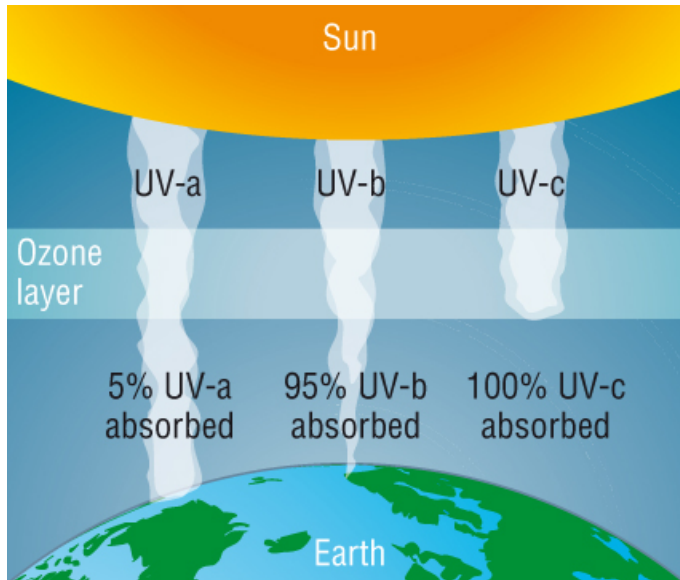
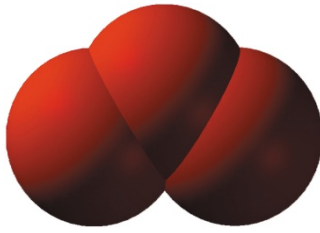
Thomas Midgley

- From the late 1800's to the 1930's gases like ammonia, chloromethane and sulphur dioxide was used as refrigerants.
- 2 of these gases are toxic and when the refrigerators (and air conditioning) leaked, people would die!!
- Thomas Midgley developed a non toxic refrigerant, freon (CCl_2F_2) or CFC's.
- He famously demonstrated the non toxic nature by inhaling the gas and extinguishing a flame by slowly exhaling over it.
- These were used as coolants in refrigerators, aerosol propellants and blowing agents.
- They were also used as blowing agents - the gas in expanded polystyrene foam (now replaced with CO_2).

Trouble with CFCs

- CFC's have a devastating effect on the ozone layer.
- The ozone layer filters out harmful UV light which can cause **skin cancer**.
- CFC's were used in refrigeration and aerosol propellants.
- The stability of CFC's has been the problem and the concentration has slowly built up in the atmosphere.
- In the stratosphere CFC's absorb UV light forming chlorine radicals.
- It is these chlorine radicals that break down ozone to oxygen:

The ozone layer



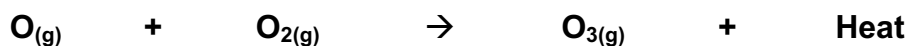
- Ozone is 3 oxygen atoms joined together.
- We are producing ozone where we don't want it and destroying it where we do want it.
- Low level ozone in the troposphere causes respiratory problems.
- The destruction of high level ozone allows harmful UV radiation to reach earth.
- Ozone acts like a big pair of sunglasses filtering out most of the harmful UV radiation.
- Prior to the formation of ozone our planet was scorched and no life could survive.
- UV radiation is divided into a, b, and c.
- C is the most harmful and is blocked out completely by ozone.
- A is the weakest and only a small amount is absorbed by ozone. This is the one that gives you a tan and ages your skin prematurely.

Ozone formation:

- The first step is the homolytic fission of an oxygen molecule by UV light:

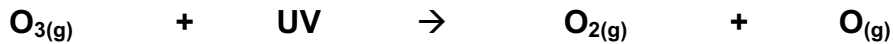


- This is an oxygen atom which contains 2 unpaired electrons, sometimes called a **di-radical**.
- The oxygen atoms reacts with oxygen molecules forming ozone. This gives out heat - exothermic:

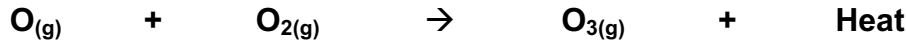


How the ozone layer works:

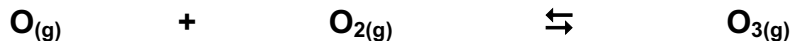
- Ozone absorbs UV radiation breaking the molecule into oxygen molecules and atoms:



- The oxygen atom then reacts with an oxygen molecule:



- Overall, UV is converted to heat energy and this process continues until the 2 reactions reach an equilibrium:



Ozone depletion

1) CFC's:

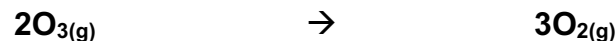
- UV light breaks the C – Cl bond releasing chlorine radical



- This chlorine radical catalyses the decomposition of ozone with the chlorine radical coming out unchanged (and available for more ozone decomposition).

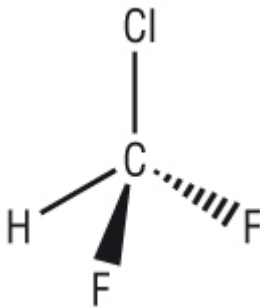


Overall



- Free radicals react fast and the chlorine radical could decompose as many as 100000 ozone molecules.
- The oxygen radical in step 2 is produced from UV dissociation of oxygen and ozone in the stratosphere.

HCFC's - alternatives to CFCs



- HCFCs are being used as a temporary replacement until something more suitable is found
- Again they are non toxic and non - flammable.
- They do still deplete ozone but are only about a tenth of the amount.

Ozone friendly products:

- Although these contain no CFCs, they usually contain hydrocarbons like butane.
- This means they are flammable - not ideal!!

Questions:

a) Explain, using chemical equations, the role of ozone in the atmosphere

b) Use a reaction mechanism to show the effects of CFC's in the atmosphere

Initiation:

Propogation:

Overall:

c) Even though the use of CFC's have been dramatically reduced over the last 4 decades, explain why there is still a hole in the ozone layer

Further Questions

- a) The relative rates of hydrolysis of the following halogenoalkanes can be determined experimentally:

Chloropropane

Bromobutane

Iodobutane

- I. Put the above halogenoalkanes in order with the most reactive first

- II. Explain their relative reactivity

- III. Describe a simple chemical experiment to show how you would determine their relative reactivity. Include any **reactions** and **observations** in your answer:

- IV. What determines whether a the halogenoalkanes undergo **substitution** or **elimination** with hydroxide ions?

In your answer include the **role of the hydroxide ion**