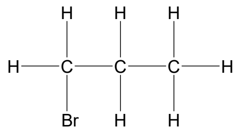
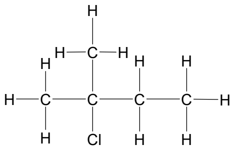
Halogenoalkanes

Naming halogenoalkanes

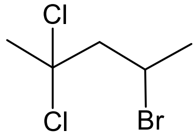
Based on original alkane, with a *prefix* indicating halogen atom:
Fluoro for F; Chloro for Cl; Bromo for Br; Iodo for I.

Substituents are listed **alphabetically**


1-bromopropane

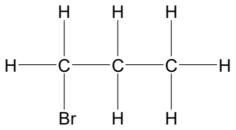

2-chloro-2-methylbutane

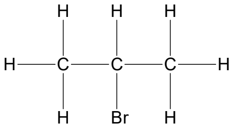
If there are two or more halogen groups then di, tri are used and each one is numbered and the groups are listed alphabetically

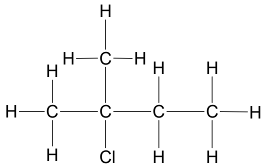

4-bromo-2,2-dichloropentane

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

Nucleophilic substitution reactions

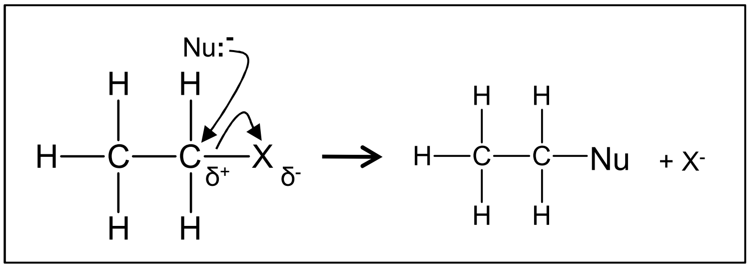
Most halogens are more electronegative than carbon and so a dipole is induced and the C-X bond is polar.

$$C^{\delta+}\text{–}F^{\delta-} > C^{\delta+}\text{–}Cl^{\delta-} > C^{\delta+}\text{–}Br^{\delta-}$$

The positive dipole on the carbon attracts nucleophiles, and the halogen atom is swapped atom for another atom or groups of atoms in a substitution reaction. The generalised mechanism shows the general mechanism for nucleophilic substitution although there are variations in the mechanism depending on whether the halogenoalkane is primary, secondary or tertiary.

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

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

:Nu represents any nucleophile – they always have a **lone pair** and act as **electron pair donators**

Rate of Nucleophilic Substitution Reactions

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

The different halogenoalkanes react at different rates. This can be observed by observing the hydrolysis reaction of the halogenoalkanes with water in a silver nitrate solution.

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

$$\mathbf{CH_3CH_2X + H_2O \rightarrow CH_3CH_2OH + X^- + H^+}$$

Aqueous silver nitrate is added to a halogenoalkane 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 halogenoalkane and so the rate of formation of the precipitate can be used to compare the reactivity of the different halogenoalkanes.

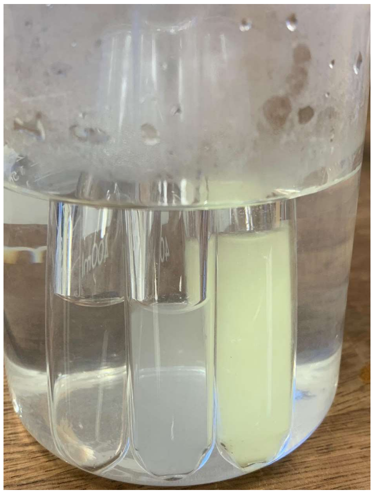
$CH_3CH_2\mathbf{I} + H_2O \rightarrow CH_3CH_2OH + \mathbf{I}^- + H^+$

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

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

$Ag\mathbf{I}_{(s)}$ - yellow precipitate
$Ag\mathbf{Br}_{(s)}$ – cream precipitate
$Ag\mathbf{Cl}_{(s)}$ – white precipitate

↑ forms faster



One might consider that the different strength of the dipoles on the C-Halogen bond might play a role in the rate of the hydrolysis reaction. The evidence does not hold up though as the one with the weakest dipole (iodine) forms fastest. So the limiting factor cannot be how well the halogenoalkane attracts the nucleophile. The factor that actually seems to explain the results if the strength of the C-Halogen 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

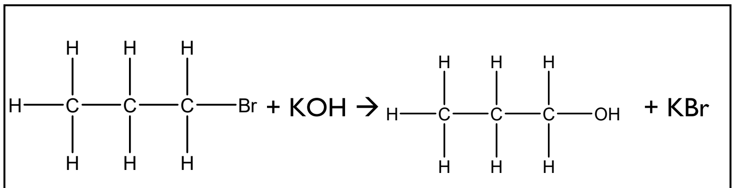
The iodoalkanes are the fastest to substitute and the fluoroalkanes are the slowest. The strength of the C-F bond is such that fluoroalkanes are very unreactive

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

Nucleophilic substitution with ***aqueous*** hydroxide ions

This is a similar reaction to the hydrolysis reaction with water but the OH^- is a stronger nucleophile than water as it has a full negative charge and so is more strongly attracted to the $C^{\delta+}$ so the reaction occurs more readily.

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

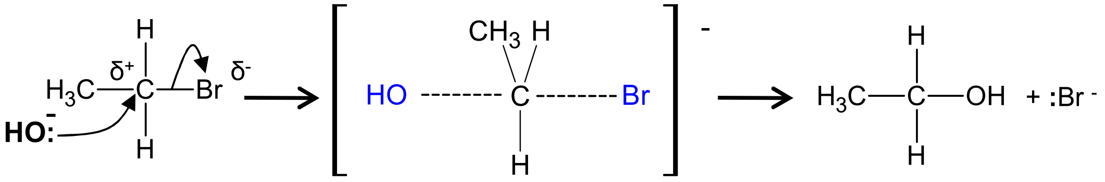


1-bromopropane   propan-1-ol

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

SN_2 nucleophilic substitution mechanism for halogenoalkanes

SN_2 The S means substation, the N means nucleophile and 2 is for two molecules in the rate determining step. This will be explained more in the reaction kinetics chapter but the slow step is the first step here.



transition state.

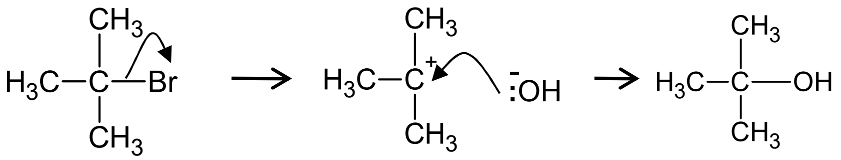
The attacking OH^- group is a nucleophile. It is attracted to the slightly positive carbon atom and has a lone pair of electrons which can form a new covalent bond to the carbon.

This mechanism goes through a **transition state**: the C-OH bond is forming at the same time as the C-Br bond is breaking

This mechanism occurs with primary halogenoalkanes

SN_1 nucleophilic substitution mechanism for tertiary halogenoalkanes

The 1 in SN_1 is for one molecules in the rate determining step. This will be explained more in the reaction kinetics chapter but the slow step is the first step here and there is only one molecule in it



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.

Primary halogenoalkanes do not do the SN_1 mechanism because they would only form an unstable primary carbocation.

See chapter 6.15 Isomerism for a discussion how these mechanism can affect optical activity in chiral compounds

Nucleophilic substitution with ammonia

This is a similar reaction to the one with hydroxide ions and converts the halogenoalkane into an amine. The conditions reflect the need to keep a high concentration of ammonia in the reaction which is not so easy because ammonia is a gas.

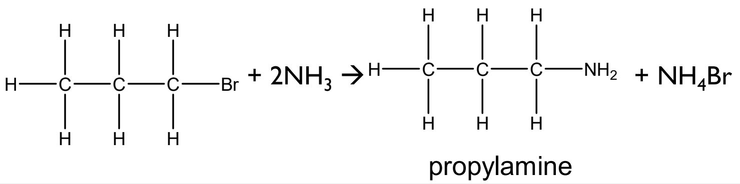
Change in functional group: **halogenoalkane → amine**

Reagent: NH_3 dissolved in ethanol

Conditions: Heating under pressure in a sealed tube

Mechanism: Nucleophilic Substitution

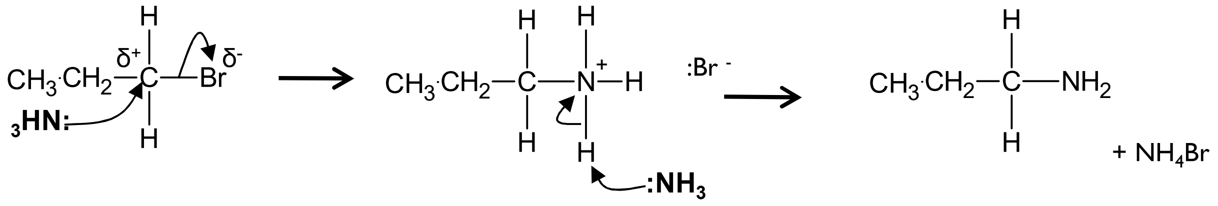
Type of reagent: Nucleophile, $:NH_3$



Naming amines:

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

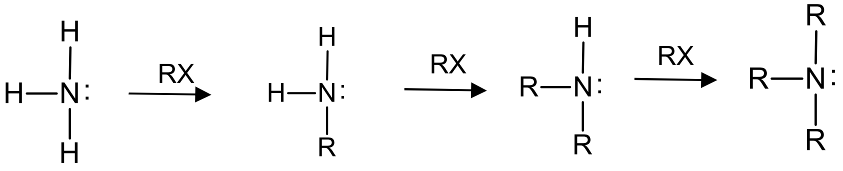
Sometimes it is easier to use the IUPAC naming for amines e.g. Prop**an-1-amine**



The reaction needs two molecules of ammonia. The first acts as a nucleophile in the first step. The second ammonia molecule acts as a base and removes a proton from the intermediate formed in step 1

Further substitution reactions can occur between the halogenoalkane and the amines formed leading to a lower yield of the amine. Each hydrogen atom on the amine can be successively removed. Using excess ammonia helps minimise this but this method will give a mixture of products.

Further reactions

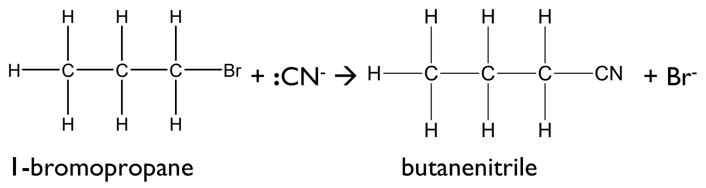


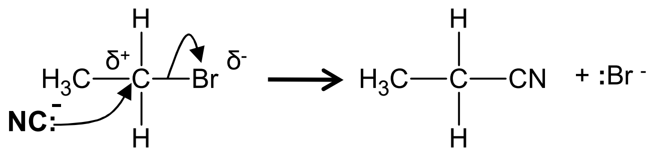
We will look at these further reactions in more detail in the chapter 6.10 amines

Nucleophilic substitution with cyanide ions

This is another similar substitution reaction swapping the halogenoalkane for a nitrile groups. This is an important reaction in organic synthesis because it can be used to increase the length of the carbon chain. The nitrile group can be hydrolysed to carboxylic acid group or reduced to an amine group so adding a nitrile group on to a chain can be an important step in building up new organic molecules.

Change in functional group: halogenoalkane → nitrile
Reagent: KCN dissolved in **ethanol/water mixture**
Conditions: Heating under reflux
Mechanism: Nucleophilic Substitution
Type of reagent: Nucleophile, $:CN^-$





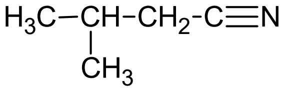
This reaction increases the length of the carbon chain (which is reflected in the name) In the above example butanenitrile includes the C in the nitrile group

Note: the mechanism is identical to hydroxide ion one

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



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

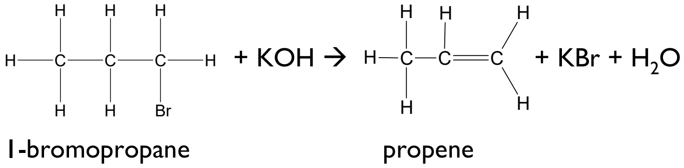
Note the naming: but**ane**nitrile and not butannitrile.

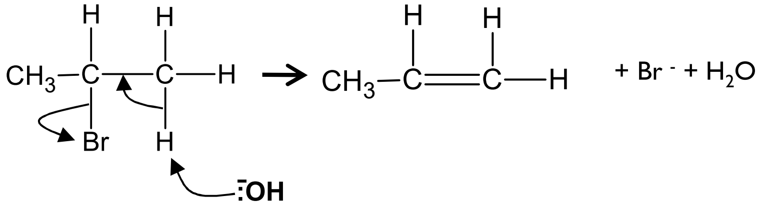
Elimination reaction of halogenoalkanes

Halogenoalkanes can also be converted to alkenes by an elimination reaction which can be defined as the removal of small molecule (often water) from the organic molecule. The reagent of potassium hydroxide is the same one as used for the substitution reaction. The conditions here are vital. Using ethanol as a solvent for the KOH instead of water will promote the elimination reaction. Often though a mixture of products from both elimination and substitution occurs

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^-





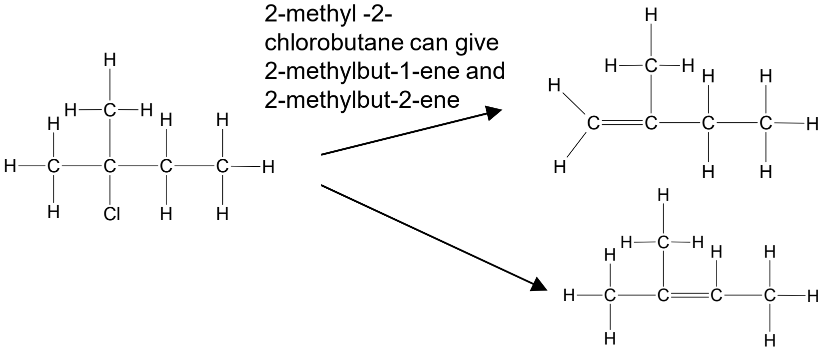
The hydroxide ion, OH^-, acts as a base and removes a proton from a carbon atom adjacent to the one bonded to the bromine. The two electrons in the C-H bond move to form the Pi bond to make the alkene, and the C-Br bond breaks.

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

Aqueous: substitution

Alcoholic: elimination

With unsymmetrical secondary and tertiary halogenoalkanes two (or sometimes three) different structural isomers can be formed because there is more than one different hydrogen atoms on adjacent carbon atoms



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

Grignard Reactions

Grignard Reagents are used to increase the length of the carbon chain in a molecule

Preparing Grignard Reagent

A halogenoalkane is dissolved in dry ether and reacted with magnesium to produce the reactive Grignard Reagent

$CH_3CH_2I + Mg \rightarrow CH_3CH_2MgI$

ethyl magnesium iodide
Grignard Reagent

This Grignard reagent is highly reactive and the alkyl group can be considered to have a negative charge. The R^- $[^+MgI]$ and so contains a nucleophilic carbon atom

Reactions of Grignard Reagent

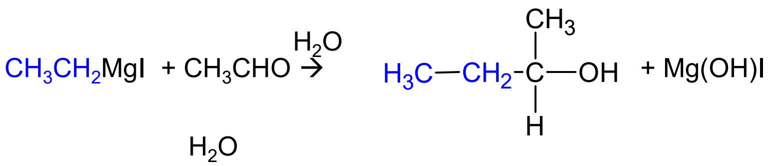
Reactions with carbonyls

With methanal will produce a **primary alcohol**

$$CH_3CH_2MgI + HCHO \xrightarrow{H_2O} CH_3CH_2CH_2OH + Mg(OH)I$$

$$RMgI + HCHO \rightarrow RCH_2OH + Mg(OH)I$$

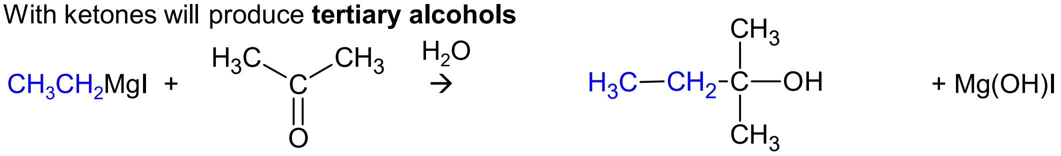
With other aldehydes will produce **secondary alcohols**



$$CH_3CH_2MgI + CH_3CHO \xrightarrow{H_2O} H_3C-CH_2-\underset{H}{\overset{CH_3}{C}}-OH + Mg(OH)I$$

$$RMgI + R'CHO \xrightarrow{H_2O} RCH(OH)R' + Mg(OH)I$$

With ketones will produce **tertiary alcohols**



$$CH_3CH_2MgI + H_3C-C(=O)-CH_3 \xrightarrow{H_2O} H_3C-CH_2-\underset{CH_3}{\overset{CH_3}{C}}-OH + Mg(OH)I$$

$$RMgI + R'COR'' \xrightarrow{H_2O} RR'C(OH)R'' + Mg(OH)I$$

Reaction with carbon dioxide

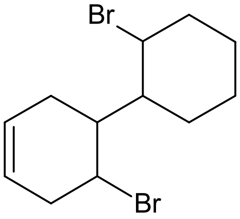
With CO_2 will produce a **carboxylic acid**

$$CH_3CH_2MgI + CO_2 \xrightarrow{H_2O} CH_3CH_2CO_2H + Mg(OH)I$$

Questions on halogenoalkanes

1) a)C_4H_9Cl has 4 structural isomers. Draw the skeletal formulae of the 4 isomers and name each one.

b) Give the molecular formula and **c**alculate the relative formula mass, M_r, of the following compound.



2) Draw **displayed formulae the organic product of the following reactions. Also name the products**
a) bromoethane + aqueous KOH
b) 2-chlorobutane + aqueous KOH
c) 1-bromopropane + NH_3
d) 2-chloro-2-methylbutane + KCN
e) 1,2-dibromopropane + aqueous KOH

3) Explain what the following terms mean
a) nucleophile
b) substitution
c) elimination
d) hydrolysis
e) base

4) A substitution reaction occurs when 2-bromopropane reacts with aqueous sodium hydroxide.
a)Draw the skeletal formula of the organic product of this reaction and give its name.
b) Name the mechanism for this reaction. Draw the mechanism out with curly arrows. Explain what each of the arrows represents.
c) Explain the role of the hydroxide ion in this reaction
d)Explain why halogenoalkanes can undergo substitution reactions with hydroxide ions whereas alkanes do not undergo this reaction

5) In an experiment, some 1-chlorobutane, 1-bromobutane and 1-iodobutane were placed in separate test tubes containing silver nitrate solution. The test tubes were put in a water bath. The halogenoalkanes reacted with the water in the silver nitrate solution. The student timed how long it took for the first appearance of the silver halide precipitate in each tube at a constant temperature. This time was used to provide a measure of the initial rate of reaction.

a) Describe the likely observations – include colour of precipitate and order of appearance of precipitates. Write ionic equations for the formation of the precipitates

b) Explain in terms of bond enthalpies the observations.

c) What is the name of the organic product formed in these reactions?

d) In this reaction the nucleophile is water. Explain why using sodium hydroxide as the reagent would lead to a faster reaction than using water.

e) In this experiment, explain why a water bath was used rather than heating the test tube containing the reaction mixture directly over a Bunsen flame.

6) Ethanenitrile can be made by reacting chloromethane with potassium cyanide.
a) Write an overall equation using structural formulae for this reaction.
b) Name and the **outline** the mechanism for this reaction.
c) Explain, in terms of bond enthalpies, why bromomethane reacts faster than chloromethane with potassium cyanide.

7) a) Write an overall equation **and** outline the mechanism for the reaction of chloromethane with an **excess** of ammonia.

b) Explain why an excess of ammonia is needed in this reaction to produce a high yield of the amine

8) When potassium hydroxide reacts with bromoethane, ethene can also be formed as well as ethanol.

a) What conditions are used to maximise the formation of the ethanol.
b) Explain why, other than safety, this method is not used in industry to make ethanol.
c) What conditions are used to maximise the formation of the ethene.

d) Name the mechanism for the reaction where the bromoethane forms ethene. Draw the mechanism out with curly arrows. Explain what each of the arrows represents

e) Explain the role of the hydroxide ion in the reaction where the bromoethane forms ethene.

9) Consider the following reaction in which an alkene is formed from a halogenoalkane.

$$\mathbf{CH_3CHBrCH_2CH_3 + KOH \rightarrow CH_3CH{=}CHCH_3 + KBr + H_2O}$$

a) Name the halogenoalkane used in this reaction.
b) What essential conditions must have been used for this reaction to occur?
c) Name and outline a mechanism for this reaction.
d) Draw structures for the E and Z stereoisomers of but-2-ene.
e) Another alkene, which is a structural isomer of but-2-ene, is also formed during this reaction.
(i) State what is meant by the term *structural isomers*.
(ii) State the type of structural isomerism shown by these two alkenes
(ii)Draw the structure of this other alkene.

10) Hot concentrated ethanolic potassium hydroxide reacts with 2-bromo-3-methylbutane to form two alkenes that are structural isomers of each other. The major product is 2-methylbut-2-ene.

a) Name and outline a mechanism for the conversion of 2-bromo-3-methylbutane into 2-methylbut-2-ene according to the equation.

$(CH_3)_2CHCHBrCH_3 + KOH \rightarrow (CH_3)_2C{=}CHCH_3 + KBr + H_2O$

b) Draw and name the **displayed formula** for the other isomer that is formed.
c) State the type of structural isomerism shown by these two alkenes
d) A small amount of the halogenoalkane undergoes the substitution reaction to form an alcohol. Draw the **skeletal formula** of the alcohol and name it

11)* Nucleophilic substitution of halogenoalkanes can undergo two different mechanisms SN1 and SN2. Outline the two different mechanisms and explain how the different mechanisms are favoured by different types of halogenoalkanes

Uses of halogenoalkanes

The halogenoalkanes have many uses although some have been phased out for environmental and safety reasons

Solvents

Chloroalkanes and chlorofluoroalkanes can be used as solvents. Tetrachloromethane CCl_4 was a common non-polar solvent for use in the laboratory

CH_3CCl_3 was used as the solvent in dry cleaning. These have now largely been phased out due to the toxicity of these compounds

Anaesthetics

Trichloromethane (Chloroform) $CHCl_3$ was one of the first anaesthetics used in Victorian times but its toxicity often result in patient death. Another anaesthetic used at the time was ether ($CH_3CH_2OCH_2CH_3$). This was much less toxic but had a very high flammability. In the mid 20th century another halogenoalkane 'Halothane' $CF_3CHBrCl$ was developed. This was much less flammable and much less toxic than the previous anaesthetics used. Today Isoflurane $CF_3CHClOCHF_2$ and Sevoflurane $(CF_3)_2CHOCHF_2$ are used

CFC's

Chlorofluorocarbons were used extensively in the late 20th century. They were non-toxic, non-reactive liquids with low flammability. They had many uses including refrigerants, aerosol propellants, and foaming agents for making expanded plastics such as those used in insulation and packaging. The stability of the CFC's caused an environmental problem because they once released they lingered in the atmosphere. Eventually they diffused into the upper atmosphere. In the upper atmosphere the were exposed to high levels of ultra-violet radiation which caused the C–Cl bonds in chlorofluorocarbons (CFCs) to break and form reactive free radicals. (The C-F bond is much harder to break than the C-Cl bond.) The chlorine free radicals then destroyed the ozone layer. This process is explored more on the next page.

Legislation to ban the use of CFCs was supported by chemists and they developed alternative chlorine-free compounds. HFCs (Hydro fluoro carbons) were developed e.g. CH_2FCF_3 to replace CFC's. These are now used for refrigerators and air-conditioners. These are safer as they do not contain the C-Cl bond so break down much more easily in the lower atmosphere where they do not cause the same problem

CFC's still concern us because CFCs are still entering the atmosphere from disused items and are still used for some purposes and by some countries.CFCs have a long lifetime in the atmosphere and it takes a long time for CFCs to reach upper atmosphere.

The Ozone Layer

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

Ozone is continuously being formed and broken down in the stratosphere by the action of ultraviolet radiation

$$O + O_2 \rightleftharpoons O_3$$

Ozone formation
UV light causes an O_2 molecule to split into free radicals

$$O_2 + \text{UV-light} \rightarrow O + O$$

When the free radical hits another O_2 molecule ozone forms

$$O + O_2 \rightarrow \mathbf{O_3}$$

Ozone depletion
This is the reverse of the formation reaction..
The energy is supplied by ultraviolet light

$$O_3 + \text{ultraviolet light} \rightarrow O_2 + O$$

There is a continuous cycle of formation and depletion of ozone

The frequency of ultra-violet light absorbed equals the frequency of biologically damaging ultra-violet radiation. These reactions therefore filter out harmful UV from reaching the Earth's surface and allow life to survive on earth.
UV light can increase risk of skin cancer and increase crop mutation.

rate of ozone formation = rate of ozone removal

So there is a constant amount of ozone in the atmosphere

Destruction of Ozone Layer

Radicals from CFCs, and NO*x* from thunderstorms or aircraft, may catalyse the breakdown of ozone

Chlorine radicals are formed in the upper atmosphere when energy from ultra-violet radiation causes C–Cl bonds in chlorofluorocarbons (CFCs) to break. The C-F bond is much harder to break than the C-Cl bond.

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

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)

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

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

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

Overall equation

$$\mathbf{2\,O_3 \rightarrow 3\,O_2}$$

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

Ozone Layer.

1) a) What is the formula of Ozone?

b) Explain how ozone is formed in the atmosphere

c) What beneficial role does the Ozone layer provide for life on Earth?

2)a) Explain how chlorine atoms are formed from chlorine-containing organic compounds in the upper atmosphere. Write an equation to show this process for a molecule of CF_3Cl

b) Why does the C-Cl bond break rather than the C-F bond in the stratosphere?

3) What is a free radical?

4) a) Write two equations that show how chlorine atoms catalyse the decomposition of ozone into oxygen.

b) Explain why the chlorine atoms can be classed as a catalyst in the decomposition of ozone into oxygen.

c) Write the overall equation for the change specified in question 4a)

d) Explain why a small amount of CFC molecules can destroy many ozone molecules

5) One of the first substances used as an anaesthetic in medicine was chloroform (trichloromethane, $CHCl_3$). By 1950, *halothane* was in common use but by 1990 this had been replaced by more acceptable anaesthetics such as *desflurane*.

$CF_3CHBrCl$	$CF_3CHFOCHF_2$
halothane	*desflurane*

a) Give the IUPAC name for halothane
b) Calculate the *M*r of halothane.
c) Calculate the percentage by mass of fluorine in halothane.
d) Give the types of intermolecular force present between molecules of liquid halothane
e) Show by using an equation how halothane could decompose to form free radicals in the atmosphere
f) Use the formulae of the two anaesthetics, *halothane* and *desflurane*, to help to explain why *desflurane* is considered to be a more environmentally acceptable anaesthetic than *halothane*.

6) $3O_2(g) \rightleftharpoons 2O_3(g)\ \Delta H = +284\ \text{kJ mol}^{-1}$

a) Use Le Chatelier's principle to explain how an increase in temperature causes an increase in the equilibrium yield of ozone.

b) Nitrogen monoxide (NO) catalyses the decomposition of ozone into oxygen.
Deduce Step 3 in the following mechanism that shows how nitrogen monoxide catalyses this decomposition.
Step 1 $O_3 \rightarrow O + O_2$
Step 2 $NO + O_3 \rightarrow NO_2 + O_2$
Step 3 ....

7) Chemists supported the legislation to ban the use of CFCs. Modern refrigerators use pentane rather than CFCs as refrigerants. These belong to the class of refrigerants that cool by change of state (typically by boiling).
(a) Suggest how these refrigerants cool by change of state.
(b) Describe characteristics or properties desirable in a refrigerant
(c) With reference to its formula, state why pentane is a more environmentally acceptable refrigerant.