

# Alkyl halides



Aerosol cans used to contain alkyl halides as propellants



Aerosol being dispensed



Fire extinguishers contain alkyl halides

Did you know that alkyl halides have been and are still around us?

## Introduction

- Alkyl halides
  - (i) are also called haloalkanes or halogenoalkanes.
  - (ii) are derivatives of alkanes that possess at least one halogen atom in their molecules.
  - (iii) have carbon-halogen bond as the functional group.
- Monoderivatives
  - (i) have the general formula  $C_nH_{2n+1}X$ , where  $X = F, Cl, Br, I$ ; and  $n = 1, 2, 3, \dots$   
They are sometimes simply represented by the general formula  $R-X$  where  $R$  represents an alkyl group.
  - (ii) can be classified as:

(a) primary;  $R - CH_2X$  e.g.  $CH_3Cl$ ,  $CH_3CH_2Br$  and  $CH_3CH_2CH_2I$

(b) secondary:  $\begin{matrix} R \\ \diagup \\ C \\ \diagdown \\ R' \end{matrix} HX$  e.g.  $(CH_3)_2CHCl$ ,  $CH_3\underset{\text{I}}{\underset{|}{CH}}CH_2CH_3$

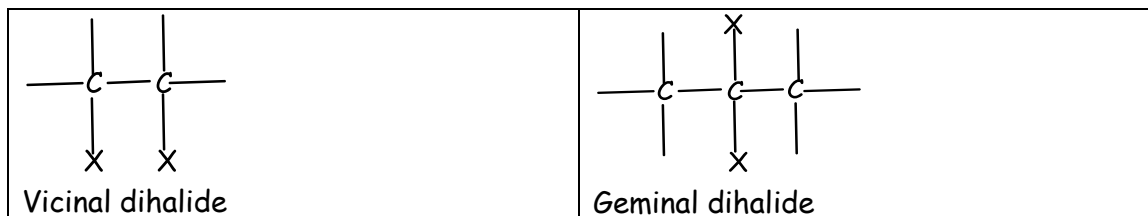
(c) tertiary:  $\begin{matrix} R \\ \diagup \\ C \\ \diagdown \\ R \end{matrix} - X$  e.g.  $(CH_3)_3C-Br$ ,  $(CH_3)_2\overset{Cl}{\underset{|}{C}}CH_2CH_3$

$R$ ,  $R^I$  and  $R^{II}$  may be identical or not.

- Polyhalides are alkyl halides which contain more than one halogen atom.

For example;

- (a) **Dihalides** contain two halogen atoms and maybe **vicinal dihalides**; where the two halogen atoms are attached to adjacent carbon atoms in a molecule or **geminal dihalides**; where the two halogen atoms are attached to the same carbon atom in a molecule.



- (b) **Tetrahalides** contain four halogen atoms per molecule.

For example,  $\text{CCl}_4$ ,  $\text{CF}_2\text{Cl}_2$ ,  $\text{CH}_2\text{FCF}_3$ ,  $\text{Cl}_2\text{C} = \text{CCl}_2$  e.t.c.

## Nomenclature of haloalkanes

- Haloalkanes are named as halo-substituted alkanes.
- Where necessary, the longest chain is chosen and numbered in such a way that the halogen atom gets the lowest number as possible.
- The position(s) of the halogen atom(s) and substituent(s) are indicated as before.

Examples are:

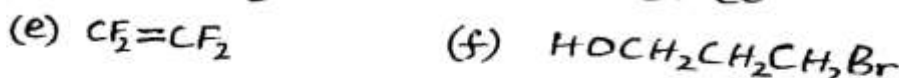
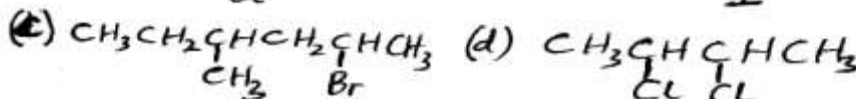
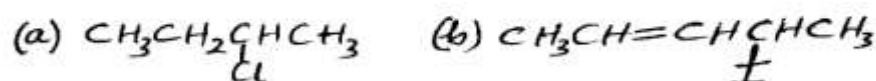
$\text{CH}_3\text{Br}$ ; bromomethane     $\text{CH}_3\text{CH}_2\text{Cl}$ ; chloroethane     $\text{CH}_3\text{CHBr}_2$ ; 1,1-dibromoethane

$\text{CH}_3\text{CH}_2\text{CH}_2\text{I}$ ; 1-iodopropane     $\text{CH}_3\underset{\text{I}}{\text{CH}}\text{CH}_3$ ; 2-iodopropane

$(\text{CH}_3)_3\text{CCl}$ ; 2-chloro-2-methylpropane

### Activity 1:

1. Name the following;



2. Write the structural formulae of the following compounds.

(a) Trichloromethane

(h) 2-iodo-2-methylpropane

(b) 1,2-dichloroethane

(i) 1-bromo-2,2-dimethylbutane

(c) 1-bromobutane

(j) 1-chloro-2-methylpropane

(d) Chloroethene	(k) 2-fluoro-2-methylpropane
(e) 3-chloro-3-methylheptane	(l) 2-bromo-4,4-dimethyloctane
(f) 1-bromopent-2-yne	(m) 4-chloropent-2-ene
(g) 1-iodobutane	(n) 2-bromo-2-methylpentane

## Isomerism in haloalkanes

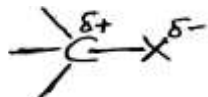
- Higher haloalkanes exhibit chain isomerism and position isomerism.

### Activity 2:

- Draw the non-cyclic isomers of a compound whose molecular formula is  $C_4H_9Cl$ . In each case give the IUPAC name and state the class of the alkyl halide.
- An organic compound **Z** on analysis was found to contain 30.30% carbon, 5.56% hydrogen and the rest being iodine. The molecular mass of **Z** was found to be 197.9.
  - Determine the molecular formula of **Z**.
  - Write the names and the structures of all possible isomers of **Z**.
- Draw the possible isomers of  $C_3H_6Br_2$  and in each case give the IUPAC name of the isomer.
- Draw the possible isomers of  $C_3H_7I$  and in each case give the IUPAC name of the isomers.
- A bromoalkane **Q** with general formula,  $C_nH_{2n+1}Br$  was found to contain 58.39% by mass bromine.
  - Determine the molecular formula of **Q**.
  - The bromoalkane burns with non-sooty flame. Write the names and structural formula of all the possible isomers of **Q**.
- An organic compound **T** on analysis was found to contain 35.04% carbon, 6.56% hydrogen and the rest being bromine. The vapour density of **T** was found to be 68.
  - Calculate the empirical of **T**.
  - Determine the molecular formula of **T**.
  - Write the names and the structural formulae of all possible isomers of **T**.

## Physical properties of haloalkanes

- The carbon-halogen bond in haloalkanes is **polar**; since the halogen atom is more electronegative than the carbon atom.



Thus, molecules of alkyl halides are polar. This makes the individual molecules to associate via dipole-dipole attractions.

- Alkane molecules are non-polar and the individual molecules associate via van der Waals forces of attraction.
- Because dipole-dipole interactions in haloalkanes are **stronger** than the van der Waals forces of attraction in alkanes, haloalkanes are less volatile than alkanes of comparable/similar relative molecular mass.
- For haloalkanes with corresponding alkyl groups, the boiling points increase with increase in molecular mass. Branching in the molecules affects their boiling points as already in alkanes.

For example;

Haloalkane	Chloromethane	Bromomethane	Iodomethane
Boiling point	-24	5	43

### Reason

The increase in molecular mass increases the strength of the intermolecular forces (van der Waals forces). Hence, a lot of energy must be supplied to separate the molecules for boiling to occur.

- Alkyl halides are insoluble in water. This is because they cannot form hydrogen bonds with water molecules. However, they are soluble in organic solvents.

### Activity 3:

Copy and complete the table below that gives the boiling points of some haloalkanes.

Compound	Molecular formula	Boiling point (°C)	Molecular mass
Chloromethane		-24	
Bromomethane		5	
Iodomethane		43	
Chloroethane		12.5	
Bromoethane		38	
Iodoethane		72	
1-chloropropane		47	
1-bromopropane		71	
1-iodopropane		102	

- (a) Carefully look at the table above and deduce the trend in the boiling points of alkyl halides. Predict the reason(s) for your observed trend.
- (b) Why do you think the boiling points of alkyl halides are generally higher than those of the corresponding hydrocarbons of comparable molecular masses?
- (c) 1-chlorobutane boils at  $78^{\circ}\text{C}$  while 2-chloro-2-methylpropane boils at  $51^{\circ}\text{C}$ ; yet the two compounds have the same molecular mass. Give reason(s) to support this statement.

## Methods of preparing haloalkanes

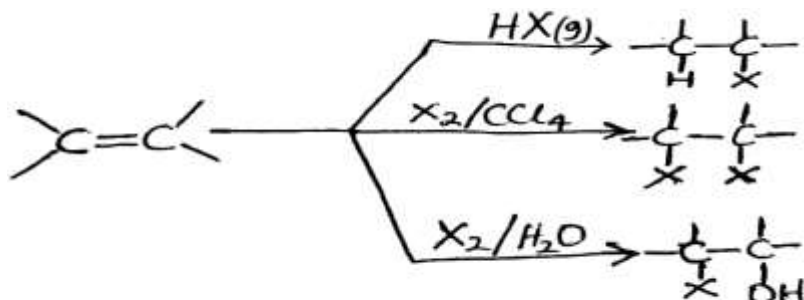
Haloalkanes can be obtained in several ways.

### A. From direct halogenation of alkanes

Refer to the reactions of alkanes for details.

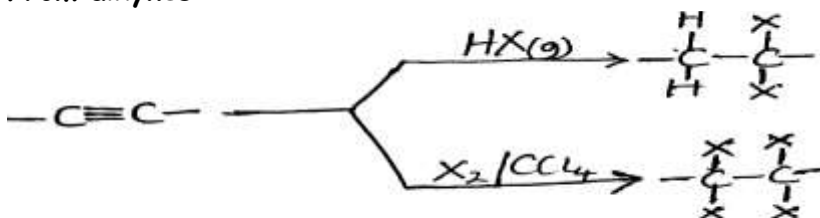
This method is not employed to make fluoroalkanes since the reaction is highly exothermic and, both fluorine and hydrogen fluoride are difficult to handle.

### B. From alkenes



Refer to the reactions of alkenes for details.

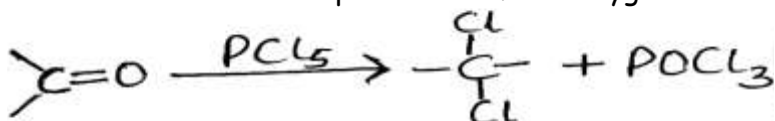
### C. From alkynes



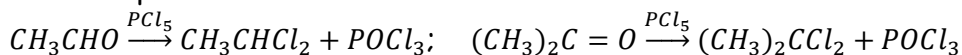
Refer to the reactions of alkynes for details.

### D. Chlorination of carbonyl compounds

The reaction involves replacement of the oxygen atom by two chlorine atoms.



For example



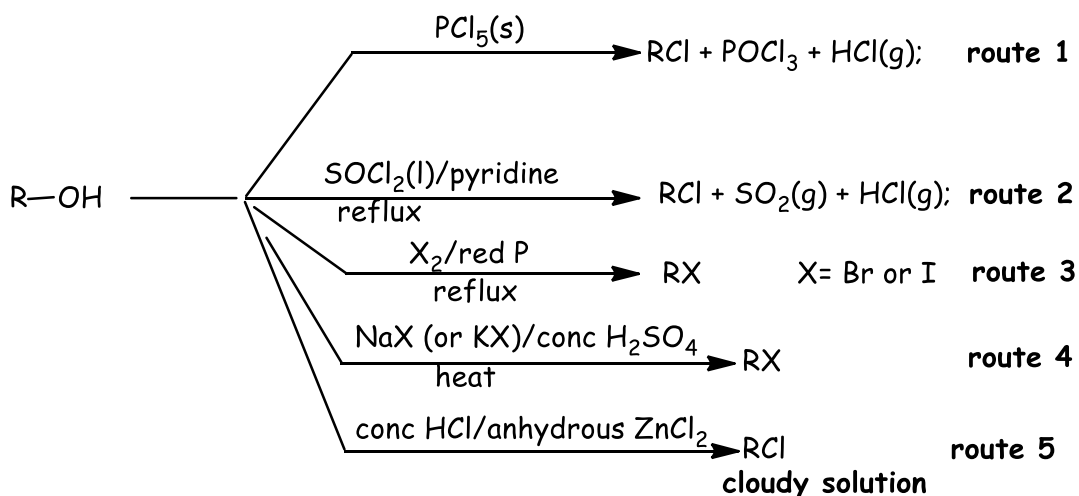
### Activity 4:

- (a) Write equation(s) to show how
- propene can be converted in 2,2-dichloropropane.
  - 2-chloropropane can be obtained from propane.
  - 1-chloropropane can be converted into propyne.
  - 2-methylpropanoic acid can be prepared from 2-chloropropane.
  - ethanol can be converted into ethyne.
- (b) Outline the mechanism for reaction leading to the formation of 2-chloropropane in (a)(ii) above.

### E. From alcohols

This involves replacement of the hydroxyl group ( $-OH$ ) in alcohols by a halogen atom ( $-X$ );  $X=Cl, Br$  or  $I$ .

The process can be effected as follows;



#### Comments about the reaction above reaction scheme

- The evolution of hydrogen chloride gas in **route 1** and **route 2** is used in organic chemistry to identify the presence of hydroxyl group ( $-OH$ ) in a compound.  
**Observations:** Misty fumes are evolved. (This is due to hydrogen chloride gas evolved).  
Pyridine in **route 2** serves to absorb hydrogen chloride as it is formed.  
The use of **route 2** is better than **route 1** because all the minor products are gaseous. Thus, much purer products are obtained.
- The use of  $X_2/red\ P$  and reflux in **route 3** is preferred for  $X = Br$  or  $I$ ; because  $PBr_5$  is not readily available and  $PI_5$  does not exist.  
A mixture of  $X_2/red\ P$  first gives  $PX_3$  ( $X=Br$  or  $I$ ), which then, reacts with the alcohol to give the haloalkane..

- In **route 4**, KX or NaX first reacts with hot concentrated sulphuric acid to generate HX(g) needed for the reaction according to the following reaction.



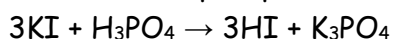
The gaseous HBr and HI formed are powerful reducing agents. Thus, they are readily oxidised by the unreacted hot acid to evolve the corresponding molecular halogens.

**Thus;**

$\text{NaBr/KBr} + \text{conc H}_2\text{SO}_4(\text{l}) \rightarrow$  gives mainly  $\text{Br}_2$  not HBr

$\text{NaI or KI} + \text{conc H}_2\text{SO}_4(\text{l}) \rightarrow$  gives mainly  $\text{I}_2$  not HI

To avoid to formation of the molecular halogens, sometimes, non-oxidizing concentrated phosphoric acid is employed in place of concentrated sulphuric acid.



- In **route 5**, a mixture of anhydrous zinc chloride and concentrated hydrochloric acid is called **Lucas reagent**.

The reaction of Lucas reagent with alcohols depends on the class of the alcohol.

Thus, Lucas reagent is used to **distinguish** between the classes of alcohols as follows:

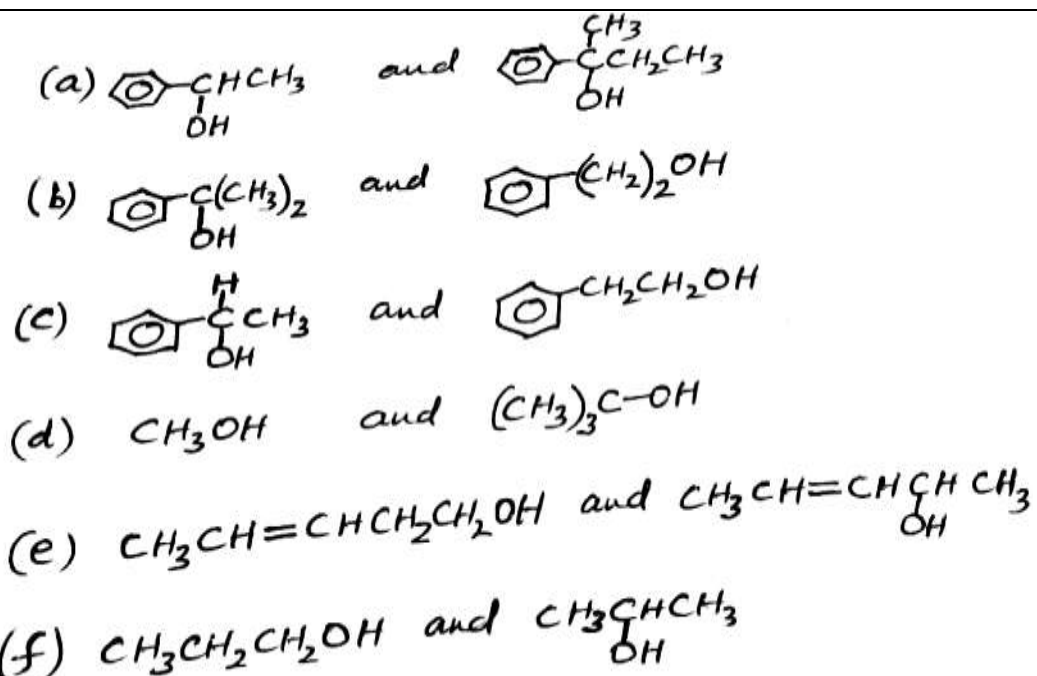
- ✓ Primary alcohols give no observable change at room temperature.
- ✓ Secondary alcohols give a cloudy solution within 5-10 minutes.
- ✓ Tertiary alcohols give a cloudy solution immediately.

**Note:**

Classes of alcohols can be identified in a similar way like the classes of haloalkanes.

### Activity 5:

1. Ethanol can be converted into chloroethane when treated with sodium chloride in the presence of hot concentrated sulphuric acid whereas treatment of ethanol with sodium iodide under similar conditions gives no iodoethane. Explain this observation.
2. Write equations to show how propene can be converted to 2,2-dichloropropane.
3. Name **one** reagent that can be used to distinguish between the following pairs of compounds. In each case, state what would be observed if each member of the pair is separately treated with the reagent you have named.



4. State the application of the following reagents in organic chemistry analysis.
  - (a) Anhydrous zinc chloride in the presence of concentrated hydrochloric acid.
  - (b) Bromine water.
  - (c) A solution of silver(I) nitrate in excess ammonia solution.
  - (d) Phosphorus(V) chloride
5. The following reagents are used to distinguish between classes of organic compounds. In each case, name the class(es) of organic compounds and state what would be observed if a member of the class is separately treated with the reagent.
  - (a) Bromine in carbon tetrachloride
  - (b) Ammoniacal copper(I) chloride solution
  - (c) Anhydrous zinc chloride in the presence of concentrated hydrochloric acid.

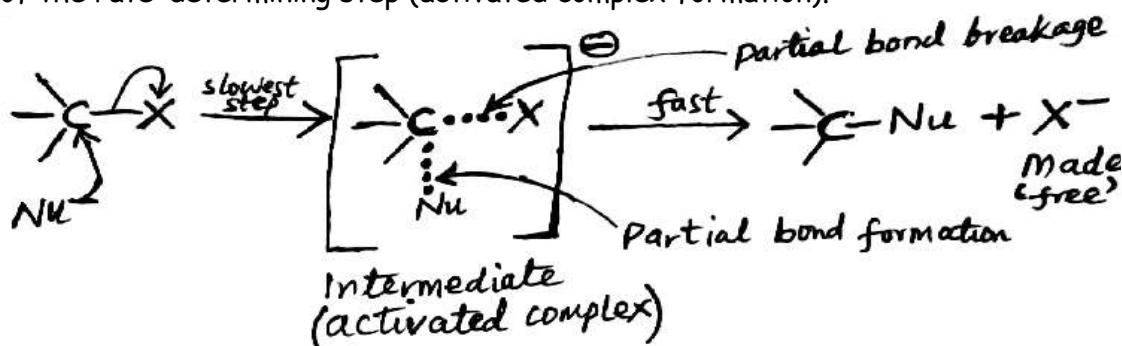
## Chemical Properties of haloalkanes

- Because the carbon-halogen bond is polar, alkyl halides are fairly reactive compounds. The partial positive charge on the carbon atom, makes it susceptible to attack by nucleophiles (electron deficient species).
- Thus, haloalkanes majorly undergo nucleophile substitution reactions; the nucleophile attacks the electron deficient carbon atom.



- The type of substitution mechanism depends on the class of the alkyl halide (i.e. the structure of the molecule).
- (a) Primary alkyl halides undergo substitution nucleophilic bimolecular ( $S_N2$ ) mechanism in substitution reactions.

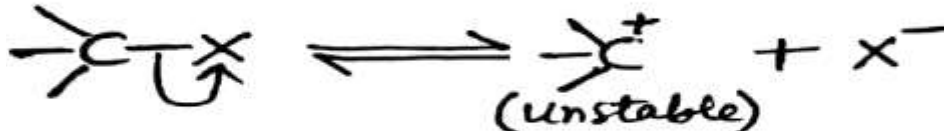
$S_N2$  refers to a reaction in which two molecules are involved in the transition state of the rate-determining step (activated complex formation).



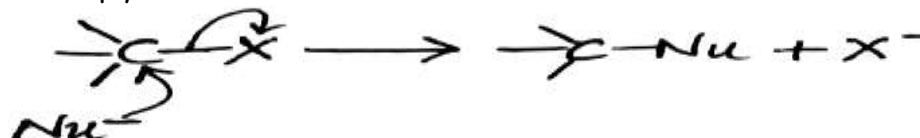
The transition state shows partial C–nucleophile bond formation and partial C–halogen bond cleavage

Why  $S_N2$  mechanism in primary alkyl halides?

- ✓ The electron deficient carbon atom is less sterically hindered. This allows the existence of five bonds on the same carbon atom in the intermediate.
- ✓ They form very unstable carbocations as intermediates.



Or simply as follows:

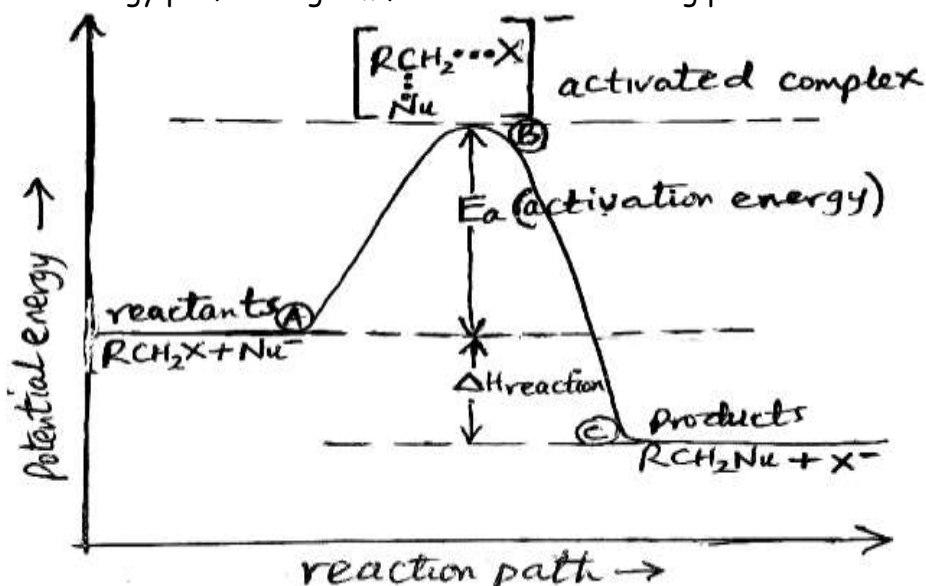


Experiments show that this reaction follows second order kinetics. That is the rate of reaction is dependent upon the concentration of both the haloalkane and the nucleophile.

The rate law/rate equation can be written as:

$Rate = k [RCH_2 - X][Nu^-]$ ; where  $k$  is called the velocity constant or rate constant and  $[ ]$  denotes concentration in moles per  $dm^3$ .

The energy profile diagram for the reaction taking place is as below:



The question that now arises is why the shape of the graph above?

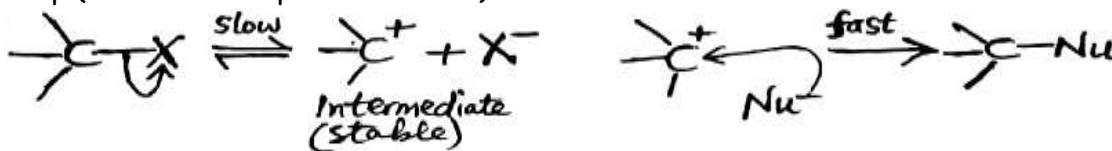
To help answer the question on the shape of the above graph, you should recall that breaking a bond requires energy while forming a bond releases energy.

#### Explanation

The potential energy of the system initially rises along AB because more energy is used to break the carbon–halogen bond than what is released during carbon–nucleophile bond formation. At B, a maximum potential is reached when carbon–halogen bond is partially broken and carbon–nucleophile bond is partially formed. This state is called the **transition state** or **activated complex**. The energy barrier,  $E_a$ , which must be overcome in order that the transition state is reached, is called the **activation energy** of the reaction. The potential energy of the system then falls along BC owing to energy released due to completion of formation of the carbon–nucleophile bond.

- (b) Tertiary alkyl halides undergo substitution nucleophilic unimolecular ( $S_N1$ ) mechanism in substitution reactions.

$S_N1$  refers to a reaction in which one molecule is involved in the rate determining step (activated complex formation).



Why  $S_N1$  mechanism in tertiary alkyl halides?

- ✓ The electron deficient carbon atom is sterically hindered. Thus, the halogen atom must leave before the nucleophile attacks.
- ✓ They form very relatively very carbocations as intermediates.

Experiments show that this reaction follows a first order kinetics. That's is the rate of the reaction is dependent upon the concentration of **only** the haloalkane. The rate law can be expressed as:  $\text{Rate} = k[\text{haloalkane}]$

### Research work

Draw a potential energy against reaction co-ordinate for substitution reactions in tertiary alkyl halides.

(c) Secondary alkyl halides are intermediate in behaviour between primary and tertiary; with  $S_N2$  mechanism predominating.

- The order of reactivity for the **same** alkyl group towards nucleophiles is such that *iodoalkanes* > *bromoalkanes* > *chloroalkanes*. For example, iodomethane reacts faster than bromomethane which in turn reacts faster chloromethane.

### Reason

The order of reactivity depends on the carbon–halogen bond strength which in turns depends on both the atomic radius and the electronegativity of the halogen atoms. Atomic radius of the halogen atom increases from chlorine atom to iodine atom. The carbon–halogen bond length increases in the order  $C - Cl < C - Br < C - I$  and hence, carbon–halogen bond strength decreases in the order  $C - Cl > C - Br > C - I$ . The iodine atom is more easily substituted followed by the bromine atom and the chlorine atom is the least easily substituted in a molecule. Hence, the observed trend. Also, the more electronegative the halogen atom is, the greater the separation of charges between the carbon atom and halogen atom (i.e. the more polar the carbon–halogen atom) and the stronger the carbon–halogen bond.

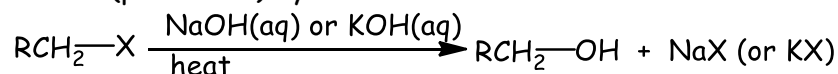
The bond length and energy for the  $C - X$  bond are:

Bond	$C - Cl$	$C - Br$	$C - I$
Bond length (nm)	0.177	0.194	0.214
Bond energy ( $\text{kJ mol}^{-1}$ )	338	276	238

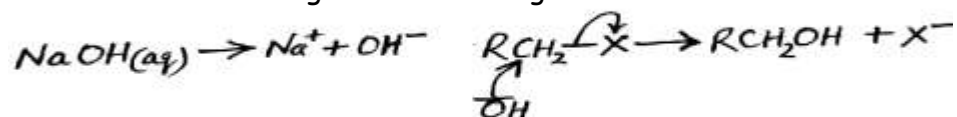
- Alkyl halides also specifically undergo nucleophilic substitution reactions because the halogen atoms are good leaving groups.
- Examples of substitution reactions in haloalkanes are:

### A. Hydrolysis (alcohol formation)

Hydrolysis of primary or secondary alkyl halides can effected by use of hot aqueous sodium (potassium) hydroxide solution.



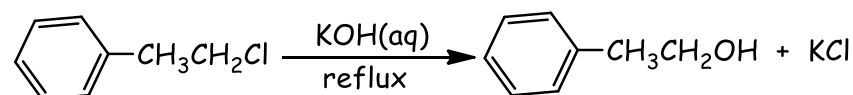
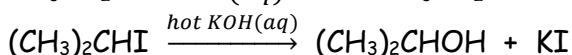
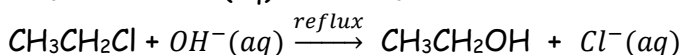
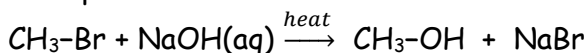
The reaction according to the following mechanism:



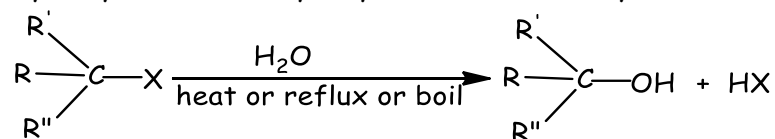
Rate law/rate equation for the hydrolysis of primary alkyl halides is

$$\text{Rate} = k [\text{RCH}_2-\text{X}][\text{OH}^-]$$

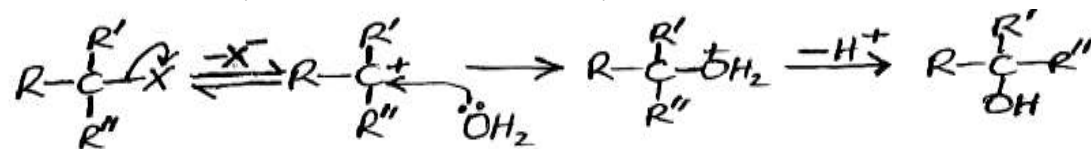
Examples:



Hydrolysis of tertiary alkyl halides is done by water alone; no base is needed.

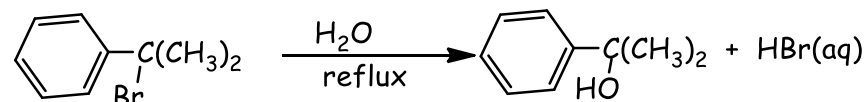
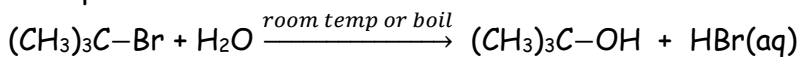


The mechanism of the above reaction is as follows:



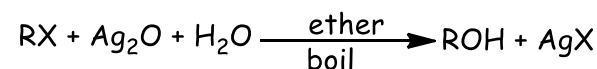
$$\text{Rate law/rate equation is Rate} = k \left[ \text{R}-\underset{\text{R}''}{\overset{\text{R}'}{\text{C}}}-\text{X} \right]$$

Examples:



Hydrolysis reaction is used in organic chemistry to prepare alcohols.

The different classes of haloalkanes give better yields of alcohols when hydrolysed using hot moist silver(I) oxide.

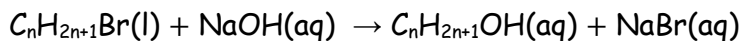


## Activity 6

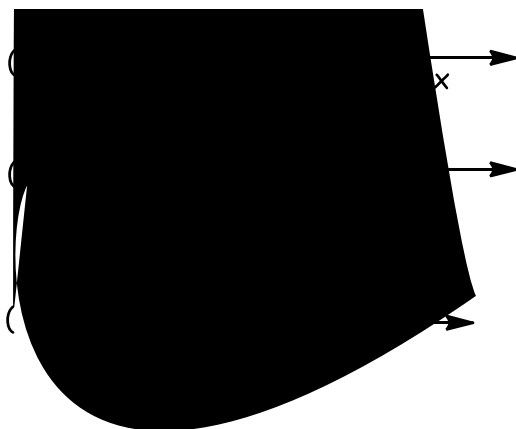
1. 1.64 g of bromoalkane, **T** ( $C_nH_{2n+1}Br$ ) was heated with excess sodium hydroxide solution. The resultant solution was cooled, acidified with dilute nitric acid and diluted to  $100\text{ cm}^3$ .

$10.0\text{ cm}^3$  of the acidified solution required  $13.0\text{ cm}^3$  of  $0.1\text{ M}$  silver nitrate solution for complete reaction.

**T** reacts with hot sodium hydroxide solution according to the following equation.

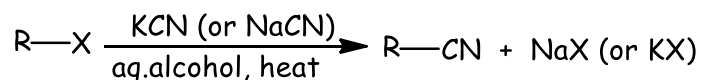


- (a) State what was observed when the resultant solution was treated with silver nitrate solution. Give a reason for your answer.
  - (b) Calculate the molecular mass of **T**.
  - (c) Deduce the molecular formula of **T**. ( $Br = 80$ )
  - (d) Write the structural formulae and IUPAC names of all the possible isomers of **T**.
  - (e) Write equation to show how **T** can be
    - (i) obtained from ethanol.
    - (ii) converted to poly(propene).
2. Complete the following equations and in each case outline a mechanism for the reaction.



### B. Nitrile formation

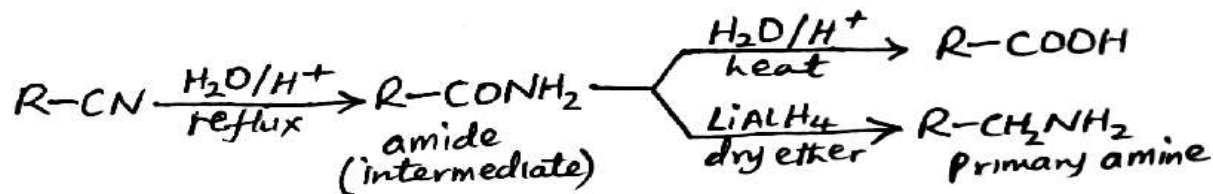
The process can be effected as follows:



Aqueous alcohol serves as a solvent; the water component dissolves the alkali metal cyanide and the alcohol dissolves the haloalkane.

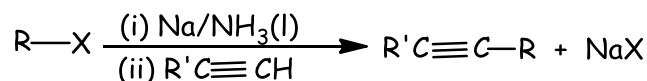
In this case, the nucleophile is the cyanide anion,  $N \equiv C^-$  or simply  $^-\text{CN}$

The nitriles are useful compounds in organic synthesis and can be used as follows:



Nitrile formation is used in organic synthesis to increase the length of the carbon chain.

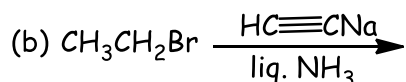
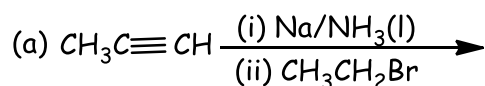
### C. Formation of higher alkynes



Refer to preparation of alkynes for details.

#### Activity 7

1. Complete the following equation and outline a mechanism for the reaction.



2. Write equations to show how the following conversions can be effected.

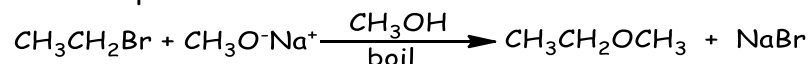
- Pent-2-yne can be obtained from calcium carbide.
- Ethene can be converted in pentane.
- Propan-1-ol can be converted into but-2-ene.

### D. Ether formation (Williamson's synthesis)

Ethers are organic compounds with the structure,  $R-O-R'$ .

They formed when the haloalkane is refluxed/boiled with alcoholic solution of sodium (or potassium) alkoxide.

For example;

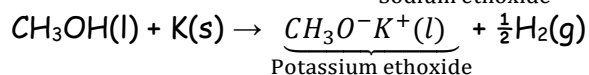
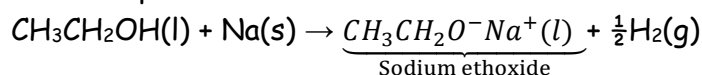


The nucleophile is the alkoxide ion,  $R'O^-$ .

**Note:**

- $R'O^-K^+$  and  $R'O^-Na^+$  are called potassium alkoxide and sodium alkoxide respectively. The alkoxides are made by dissolving the alkali metal in excess of the appropriate alcohol.

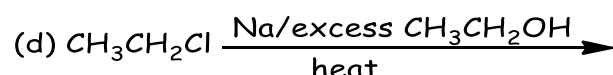
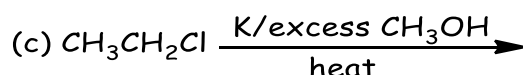
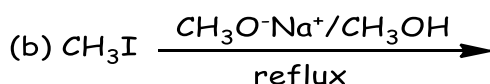
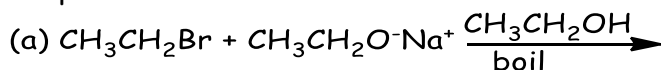
For example:



- Alkyl halides also form ethers when reacted with dry silver(I) oxide ( $Ag_2O$ ).  
For example:  $2CH_3CH_2Br + Ag_2O(s) \rightarrow CH_3CH_2-O-CH_2CH_3 + 2AgBr$
- This reaction is used in organic chemistry for preparation of both symmetrical and unsymmetrical ethers.

**Activity 8**

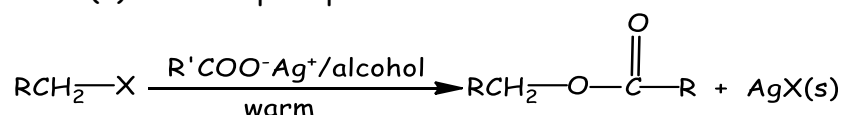
Complete and outline the mechanism for each of the following reactions.



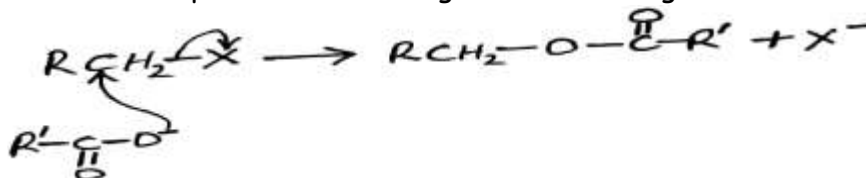
**E. Ester formation**

It involves reacting the haloalkane with silver(I) salt of a carboxylic acid in an alcohol as a solvent.

Silver(I) halide is precipitated in this reaction.

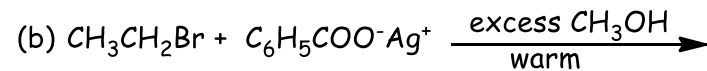
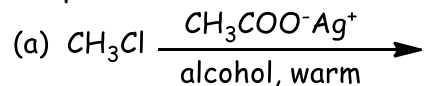


The reaction proceeds according to the following mechanism.



### Activity 9

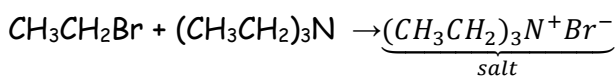
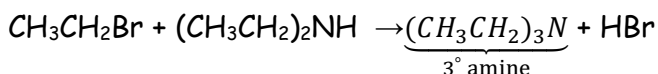
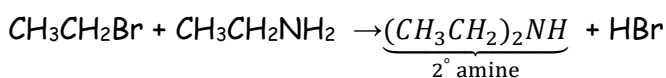
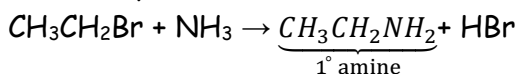
Complete and outline the mechanism for each of the following reactions.



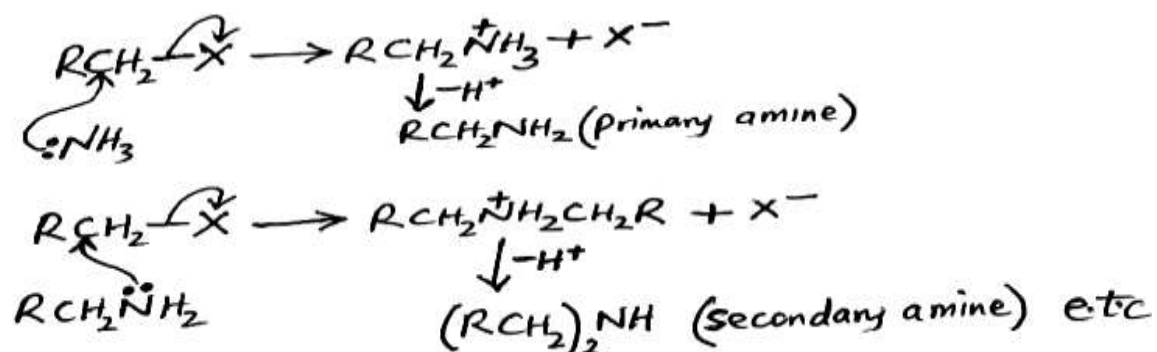
### F. Formation of amines

A mixture of amines is formed when alkyl halides are heated with alcoholic solution of ammonia in a sealed tube at 100°C. A mixture of products is formed because products formed are more reactive than ammonia.

For example:



The mechanism for this reaction can be outlined as below:



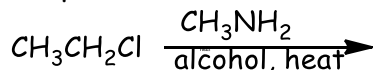
#### Note:

Ammonia molecules are neutral nucleophiles which initiate the reaction.



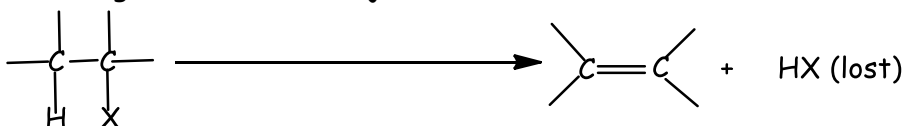
### Activity 10

- (a) Predict the formulae of the products of the reaction between excess bromopropane and hot alcoholic ammonia. Give reason(s) for your answers.
- (b) Complete the following reaction.
- $$\text{CH}_3\text{Br} + \text{hot excess NH}_3 \xrightarrow{\text{ethanol}}$$
- (c) Outline the reaction mechanism and give a reason for the choice of product in the reaction in (b) above.
- (d) Complete and outline the mechanism for the following reaction.



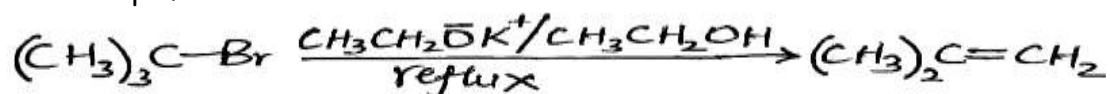
### Elimination reactions of alkyl halides

- Alkyl halides also undergo elimination reactions which involve the removal of hydrogen and halogen atoms from adjacent carbon atoms. An alkene is formed.



- Conditions for the reaction are; KOH, excess alcohol (ethanol/methanol) and heat (reflux)
- In this reaction,
  - $\text{CH}_3\text{CH}_2\text{X}$  (X=Cl, Br or I) gives poor yield of ethene.
  - much better yields of alkene can be obtained from secondary, tertiary or higher primary alkyl halides.
- Elimination reactions proceed either via **E1** or **E2 mechanism** depending on the structure of the alkyl halide (i.e. whether the alkyl halide is 1°, 2° or 3°).
- E1 mechanism**; means elimination unimolecular, referring to a reaction in which only one molecule is involved in the rate determining step (slowest step of the reaction). Experiments show that this type of reaction mechanism is mainly followed by tertiary alkyl halides.

For example;



The rate of reaction being dependent upon the concentration of only the haloalkane.

Thus, we can say the reaction follows a *first order kinetics*.

The mechanism of the reaction can be outlined as follows:

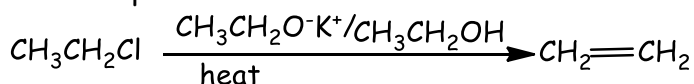
<b>Step 1:</b>	<p>This involves heterolytic cleavage of carbon–halogen bond. It is the slowest step and the rate determining step of the reaction.</p> $(CH_3)_3C-Br \rightleftharpoons (CH_3)_3C^+ + Br^-$
<b>Step 2:</b>	<p>The ethoxide ion abstracts a proton from the carbonium ion formed in step 1 with formation of carbon–carbon double bond.</p> $(CH_3)_3C^+ + CH_3CH_2O^- \longrightarrow (CH_3)_2C=CH_2 + CH_3CH_2OH$

- **E2 mechanism** means elimination bimolecular. It refers to a reaction in which two molecules are involved in the rate determining step of the reaction. Thus, it is a one–step reaction.

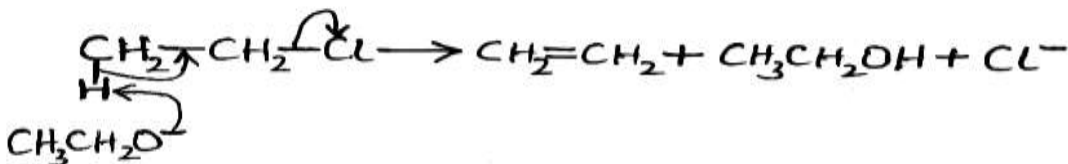
This reaction follows a *second order kinetics*; meaning that the rate of reaction is dependent upon the concentration of both the base and the alkyl halide.

Experiments show that this type of reaction mechanism is mainly followed by primary alkyl halides.

For example:



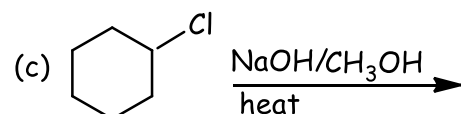
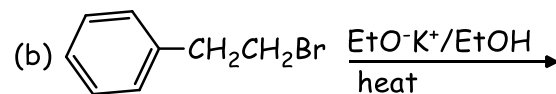
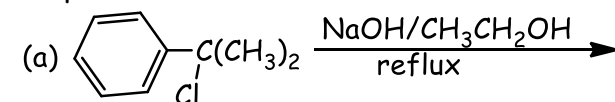
The mechanism of the reaction can be outlined as follows:

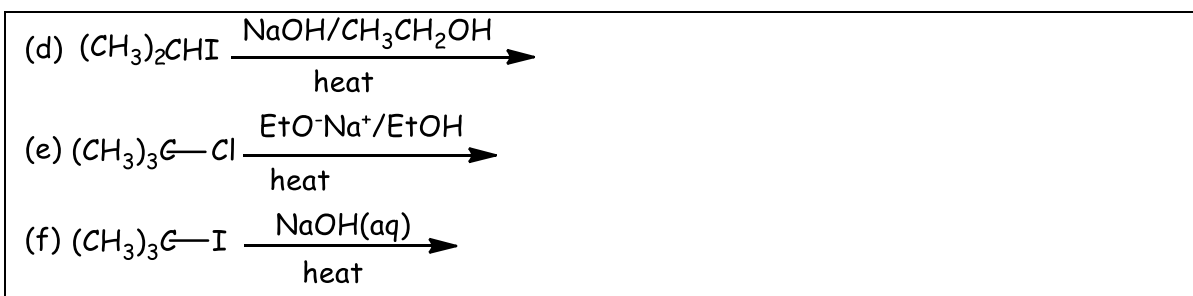


- Secondary alkyl halides are intermediate in behaviour; thus, they can either follow E1 or E2.

### Activity 11

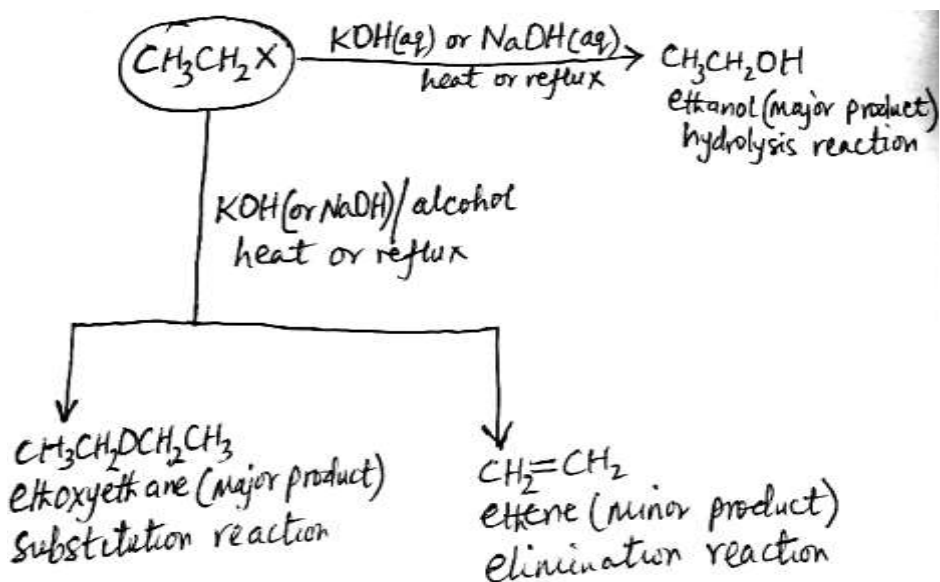
Complete and outline the mechanism for each of the following reactions.





### Concurrent substitution and elimination

- Elimination reaction usually occurs in competition with substitution reaction. Thus, we have E1 versus S<sub>N</sub>1 and E2 versus S<sub>N</sub>2.
- The percentage yield of the product depends on a number of factors namely:
  - (i) Temperature at which the reaction is carried out; higher temperatures favour elimination reaction. Thus if substitution product is desired, the reaction temperature should be low
  - (ii) The type of alkyl halide used in the reaction; sterically hindered substrate favours the elimination product. Thus, elimination reaction becomes progressively more important in the order  
primary haloalkane < secondary haloalkane < tertiary haloalkane
  - (iii) Solvent used.
- The effect of solvent used can be best illustrated by treating the alkyl halide with an alkali; hydroxide ions.
  - (a) In aqueous solution i.e.  $\text{KOH(aq)}$ ,  $\text{NaOH(aq)}$  or  $\text{OH}^-(\text{aq})$   
 Primary haloalkanes undergo substitution reaction while tertiary haloalkanes undergo elimination reaction.  
 This explains why hydrolysis of tertiary haloalkanes to form alcohols can be best done using water alone. This is because water is a much weaker nucleophile than the hydroxide ions.
  - (b) In alcoholic solution i.e.  $\text{KOH/alcohol}$ ,  $\text{NaOH/alcohol}$  or  $\text{OH}^-/\text{alcohol}$   
 Lower primary haloalkanes (particularly those with two carbon atoms) undergo substitution reaction while higher primary haloalkanes under elimination reaction.  
 Tertiary haloalkanes undergo elimination reaction.
- Illustration of competition between S<sub>N</sub>2 and E2 in  $\text{CH}_3\text{CH}_2\text{X}$  is as follows:



## Other reactions of haloalkanes

- The Wurtz reaction

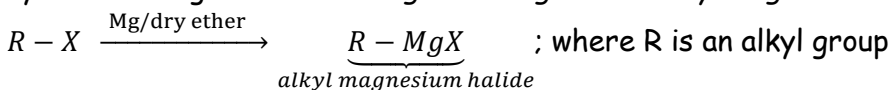
Alkyl halides react with sodium metal in dry ether to yield alkanes.

For example:  $2\text{CH}_3\text{CH}_2\text{Br} + 2\text{Na} \xrightarrow{\text{dry ether}} \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3 + 2\text{NaBr}$

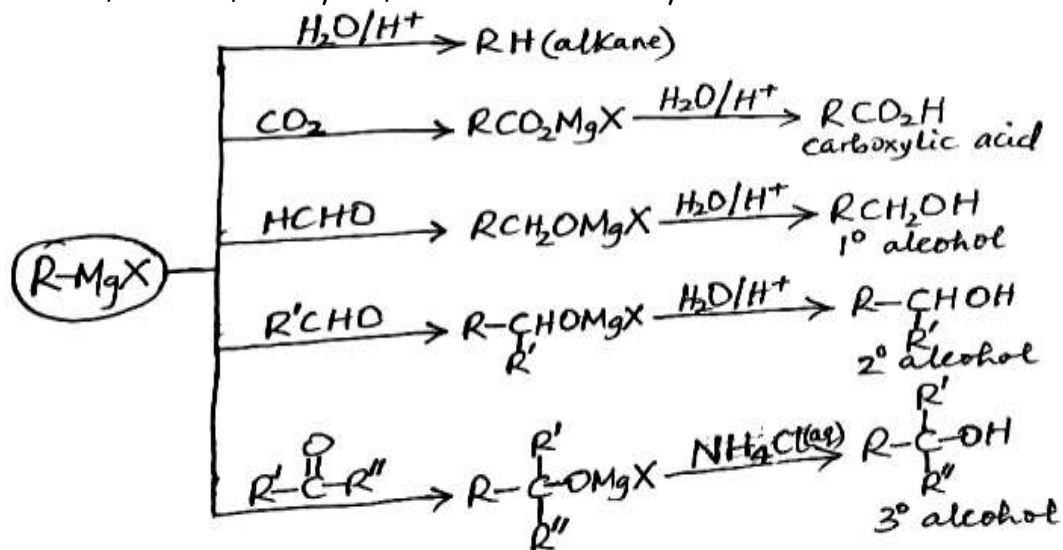
Refer to alkanes for details.

- Formation of Grignard reagents

Haloalkanes react with magnesium turnings/granules in dry ether to form useful synthetic reagents called *Grignard reagents* or *alkyl magnesium halides*.



- The alkyl magnesium halides are very reactive and are readily converted into alkanes, alkenes, alcohols, aldehydes, ketones and carboxylic acids.



Aqueous ammonium chloride is used in the hydrolysis to the tertiary alcohol as the presence of an acid causes dehydration of the alcohol formed to an alkene.

### Activity 12

Show by means of equation(s) how the following conversions can be effected. In each case indicate suitable reagents and reaction conditions.

- Ethanol to butane.
- Bromomethane to 2-methylpropan-2-ol.
- Methanol to ethanol.
- Cyclohexene to cyclohexanol.
- Cyclohexanol to cyclohexanoic acid (cyclohexanecarboxylic acid).

## Testing for aliphatic haloalkanes

- Alkaline hydrolysis of aliphatic haloalkanes provides a useful means to identify aliphatic haloalkanes in the laboratory.

### Test

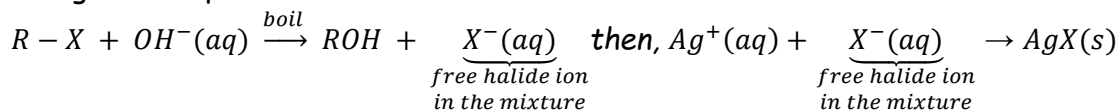
The aliphatic haloalkane is treated with aqueous sodium hydroxide solution and the mixture is refluxed/heated/boiled, and cooled. To the resultant mixture is added excess dilute nitric acid followed by silver nitrate solution.

### Observations

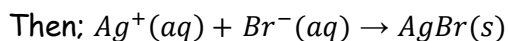
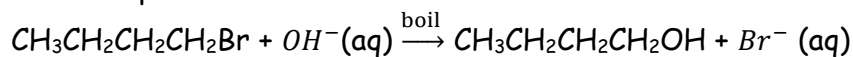
The formation of

- a white precipitate indicates a chloride ion hence a chloroalkane.
- a pale yellow precipitate indicates a bromide ion hence a bromoalkane.
- a yellow precipitate indicates an iodide ion hence an iodoalkane.

The general equations for the reactions that occur are:



For example:



### Activity 13:

1. Give reasons for each of the following procedures in testing for aliphatic haloalkanes.
  - (a) Heating the alkyl halide with aqueous sodium hydroxide solution.
  - (b) Addition of excess dilute nitric acid.
  - (c) Why dilute hydrochloric or dilute sulphuric acid is not used in place of dilute nitric acid.
2. State what would be observed and write equations for the reactions that would take place if aqueous sodium hydroxide solution followed by dilute nitric acid and silver nitrate solution were separately treated with:
  - (a) 1-chlorobutane
  - (b) 1-iodopropane
  - (c) bromocyclohexane
3. To about 3 drops of each of chloroethane, bromoethane and iodoethane in separate test tubes, was added aqueous sodium hydroxide solution. Each of the test tubes was warmed in water bath kept at  $55^{\circ}\text{C}$  for some minutes and treated with an equal amount of acidified solution of silver nitrate. The test tubes were left to stand and the time taken for the reaction to take place in the test tubes noted. The results in the test tubes were summarised as below:

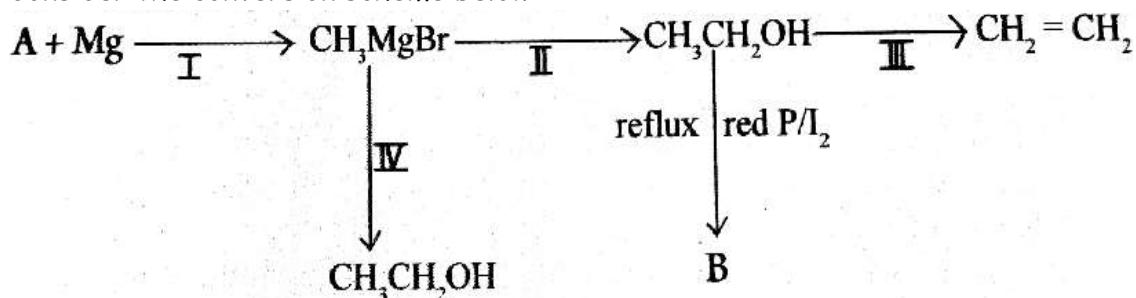
*Table of results*

Test tube	Reaction mixture	Observations
<b>I</b>	chloroethane + sodium hydroxide solution + acidified silver nitrate	white precipitate after 20 minutes
<b>II</b>	bromoethane + sodium hydroxide solution + acidified silver nitrate	pale yellow precipitate after 7 minutes
<b>III</b>	iodoethane + sodium hydroxide solution + acidified silver nitrate	immediate yellow precipitate

- (a) What name given to the type of the reaction that took place in each of the test tubes?
  - (b) Explain why the reaction in test tube **I** took a longer time whereas that in test tube **III** took the shortest time.
  - (c) Write equation and outline the mechanism for the reaction that took place in test tube **II**.
  - (d) The reaction in (c) is exothermic. Sketch a labelled potential energy versus reaction co-ordinate diagram for the reaction that took place in (c).
  - (e) Write equation(s) to show how bromoethane can be converted into
    - (i) butane.
    - (ii) butanone.
    - (iii) propan-1-ol.
    - (iv) 2-methylbutan-2-ol.
4. Discuss the difference in the reactivity of 2-bromo-2-methylbutane and 1-bromopentane with aqueous sodium hydroxide solution.

5. An aliphatic iodoalkane, **Q** contains 74.7% by mass iodine.
- Determine the molecular formula of **Q**.
  - Write down the possible isomers of **Q** and in each case identify the class of the compound.
  - Q** doesn't does not undergo  $S_N1$  reaction.
    - State what  $S_N1$  means.
    - Identify the **Q**.
  - Identify the type of reaction similar to  $S_N1$  that compound **Q** identified in (c)(ii) undergoes and state the difference between the type of reaction you have identified and the  $S_N1$  reaction.
6. Write short notes on the how haloalkanes cause global warming.
7. The boiling points of 2-chlorobutane and 2-iodobutane are 68°C and 119°C respectively. Explain this observation.
8. Discuss the reactions of iodoethane with
- benzene.
  - potassium hydroxide.
- (Include mechanisms for the reactions)
9. (a) Complete and outline the mechanism for the following reactions.
- $CH_3CH_2Cl \xrightarrow{\text{hot } KOH(aq)}$
  - $CH_3CH_2CH_2Br + OH^-(aq) \xrightarrow{\text{reflux}}$
- (b) Sketch a well labelled energy profile diagram for reaction in (a)(i) above. Explain the shape of the graph.
- (c) Write the rate law for the reaction in (a)(i) and state what would happen to the rate of the reaction if the concentration of potassium hydroxide is
- halved.
  - doubled.
- Assume in both cases the concentration of  $CH_3CH_2Cl$  is kept constant.

10. Consider the conversion scheme below:

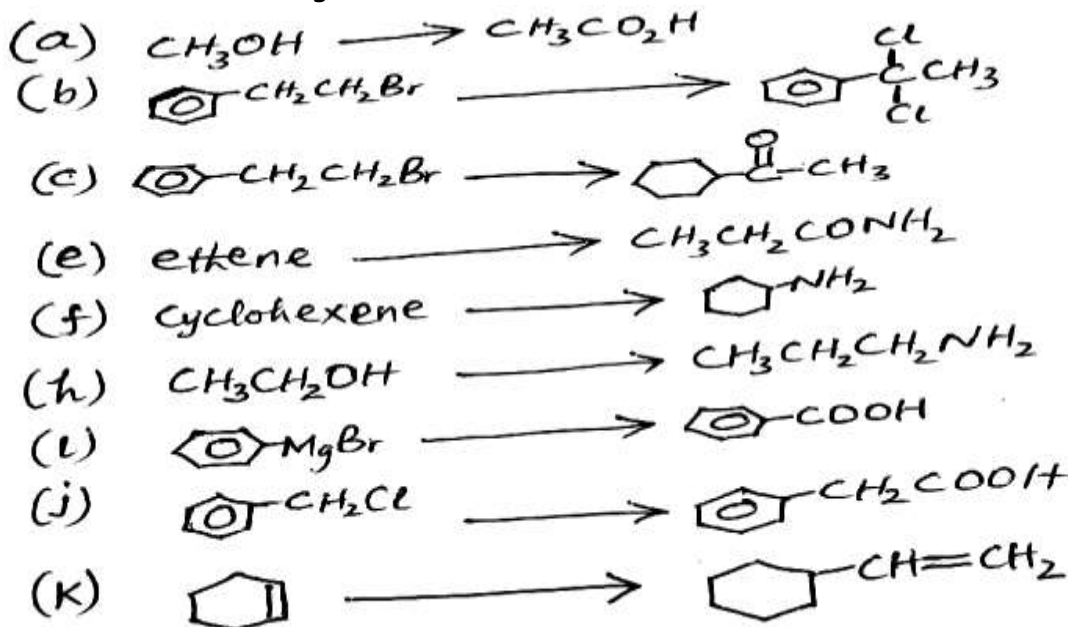


- Identify **A** and **B**.
  - State the conditions and reagents at **I**, **II**, **III** and **IV**.
  - Outline the mechanism at stage **III**.
11. (a) Write the structural formulae of the possible isomers of  $C_2H_4Cl_2$ .
- (b) Discuss briefly how one of the isomers above reacts with potassium hydroxide. Indicate the equation (s) of reactions and mechanism for the reaction.

(Your answers should include examples and where applicable the acceptable mechanisms for the reactions)

(c) Substitution reactions.

Show by means of equations only show how the following conversions can be effected. Indicate reagents and conditions for the reactions.



- Alkyl halides have wide range of uses some of which we have already mentioned.
- Alkyl halides are used:
  - as solvents for oil and grease in the dry cleaning industry and metal surfaces (e.g.  $\text{CH}_2\text{Cl}_2$  and  $\text{CCl}_2=\text{CCl}_2$  are used for this purpose while toxic  $\text{CHCl}_3$  and  $\text{CCl}_4$  have limited use for this purpose). Dichloromethane which is a chloroalkane has low toxicity and is as an excellent solvent used as a paint stripper. Chloroform is used as a solvent for organic synthesis and solvent extraction.
  - as fire-extinguishers since the compounds are non-flammable and denser; for example  $\text{CCl}_4$  whose use has been replaced by dibromochlorofluoromethane ( $\text{CBr}_2\text{ClF}$  also known as BCF) because it forms phosgene ( $\text{COCl}_2$ ), a very poisonous gas at very high temperatures.
  - as starting materials for synthesis of many important other organic compounds including some plastics. Dichlorodifluoromethane, trichlorofluoromethane and



other chlorofluoro-derivatives of methane are used as refrigerants and propellants for aerosols under the trade name of Freons.

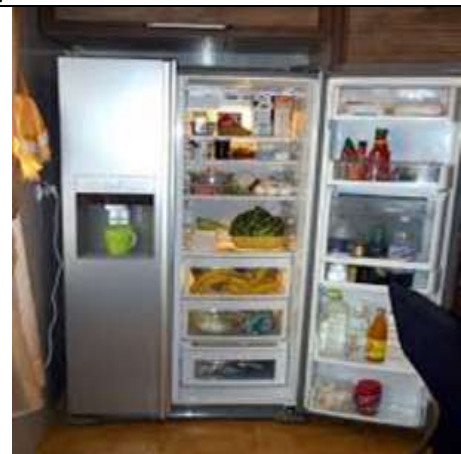
$\text{CH}_2=\text{CHCl}$  is used as anaesthetic; since its cooling effect once sprayed desensitises the nerve ending; 1-bromo-1-chloro-2,2,2-trifluoroethane ( $\text{CHBrClCHF}_3$ ) is also for this purpose.

(iv) in the manufacture of plastics e.g. PVC and Teflon

## Supplement

### The chlorofluorocarbons, CFCs

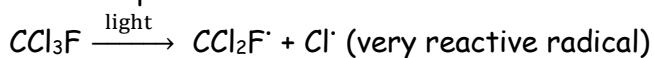
- These are haloalkanes that only contain chlorine and fluorine atoms in addition to carbon. No hydrogen atoms. Examples include;  $\text{CFCl}_3$ ,  $\text{CF}_2\text{Cl}_2$  and  $\text{CClF}_2\text{CClF}_2$ .
- CFCs were widely used as aerosol propellants, refrigerants (to replace toxic ammonia and sulphur dioxide) and solvents. Aerosols are used to dispense insecticide, hairsprays, shaving cream, perfumes, deodorants, polishes and waxes. Their use became wide spread up to around the year 1990, because they are unreactive, non-flammable, odourless, stable, non-toxic and have low boiling points.



*Old refrigerators are sources of dangerous CFCs*

- One major disadvantage of CFCs use in the environment is that they can't be removed from the atmosphere once released from the aerosol sprays or old refrigerants or any other source. This is due to their unreactive nature and being insoluble in commonly used solvents and water.
- While in the upper atmosphere (the stratosphere), a series of reactions occur in the presence of ultraviolet light to convert ozone to molecular oxygen. These reactions destroy the ozone layer which would help in absorbing the dangerous ultraviolet radiations from the sun. This results into increase in skin cancer among humans.

For example:

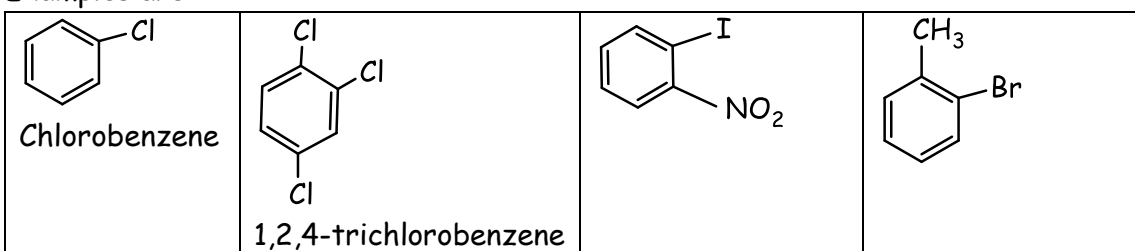


- In fact scientists have estimated that one free chlorine radical can remove one million ozone molecules.
- Because of the above dangers of CFCs, friendly haloalkanes that contain at least one hydrogen atom per molecule have been introduced. The friendly haloalkanes include;  $\text{CHClF}_2$  used in air-conditioners,  $\text{CHCl}_2\text{CF}_3$  used in blowing plastics foam, and  $\text{CH}_2\text{FCF}_3$  used in air-conditioners and refrigerators.

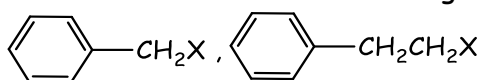
## Aryl halides

### Introduction

- Aryl halides are:
  - (i) also called hogenoarenes.
  - (ii) compounds in which the halogen atom(s) is/are directly bonded to the benzene ring.
- Examples are:



- Aromatic halides of the following form:



are **not** classified as aryl halides. They are classified as **phenyl substituted haloalkanes** or '**side-chain**' aryl halides. They resemble aliphatic haloalkanes in many of their reactions.

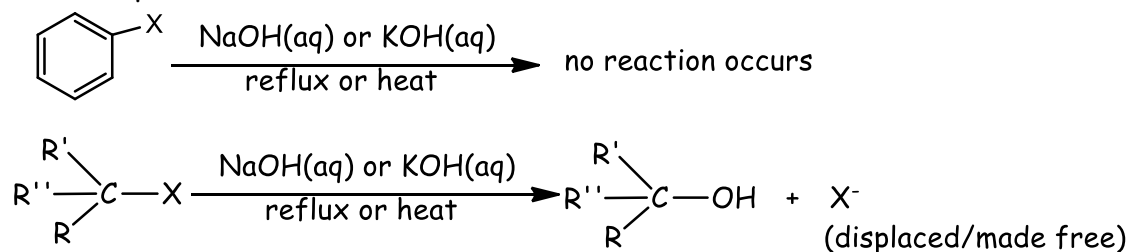
### Preparation of aryl halides

- Aryl halides can be made using the following methods:
  - (a) Direct halogenation of benzene or other aryl compounds  
Refer to the reactions of benzene for details
  - (b) Via nitrobenzene/phenylamine/diazonium salt  
Refer the formation of nitrobenzene.

## Reactions of aryl halides

- Aryl halides undergo two kinds of reaction namely:
  - Electrophilic substitution in the ring  
For details refer to notes under aromatic compounds
  - Replacement of the halogen atoms (nucleophilic substitution of the halogens)  
Under **ordinary conditions**, aryl halides do not undergo substitution reactions similar those that occur in aliphatic haloalkanes or 'side-chain' aryl halides.

For example:



R, R' and R'' may be a hydrogen atom, an alkyl group or an aryl group. The alkyl groups or aryl groups may be identical or not.

Reasons for the differences in reactivity of the two classes of halocompounds can be explained as follows:

- The carbon–halogen bond in the aryl halides is less polar and stronger. The lone pairs of electrons on the halogen atom interacts with the delocalised of pi electrons of benzene ring. This makes the carbon–halogen bond stronger and difficult to break (or This results into formation of a partial carbon–halogen double bond which makes the bond stronger and difficult to break). Thus, substitution reaction does not easily occur.
- Whereas in aliphatic haloalkanes or 'side-chain' aryl halides, the carbon–halogen bonds are polar. This because the halogen atom is more electronegative than the carbon atom. The halogen atom pulls/withdraws the bonding electrons more towards itself and this makes the carbon atom acquire partial positive charge and the halogen atom acquires partial negative charge. Therefore, the carbon atom is easily attacked by the nucleophiles and this leads to nucleophilic substitution of the halogen atom.

### Note

In 'side-chain' aryl halides, the intervening methylene/other groups prevent the interaction of the lone pairs of electrons on the halogen atom with the delocalised pi electrons of the benzene ring.

This difference in reactivity of the two classes of compounds (aryl halides versus aliphatic haloalkanes or 'side-chain' aryl halides) makes it possible to distinguish between the two classes of compounds as follows:

**Test:**

The aryl halide and aliphatic haloalkane (or 'side-chain' aryl halide) is separately treated with aqueous sodium hydroxide solution and the mixture is refluxed/heated/boiled and cooled. To the resultant mixture is added excess dilute nitric acid followed by silver nitrate solution.

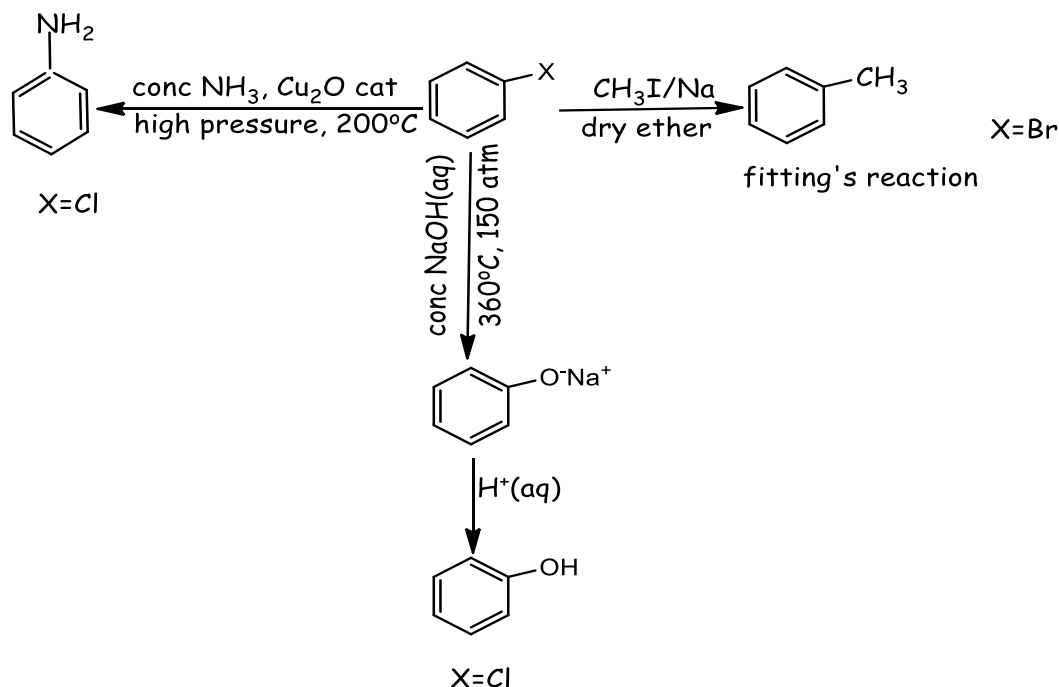
**Observations:**

The formation of

- (i) a precipitate indicates a haloalkane (or 'side-chain' aryl halide)
- (ii) no observable change indicates an aryl halide

Thus, the **reagent** is hot aqueous sodium hydroxide solution followed by dilute nitric acid and silver nitrate solution.

Some of the important substitution reactions undergone by aryl halides are summarised below:



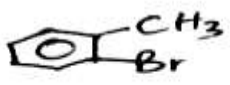
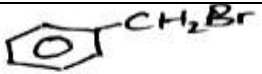



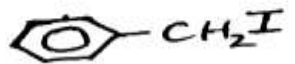


**Activity 14:**

1. Show by means of equations only show how the following conversions can be effected. Indicate reagents and conditions for the reactions.

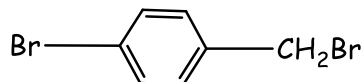
- |                                    |                               |
|------------------------------------|-------------------------------|
| (a) Propan-1-ol to butanoic acid.  | (i) Propene to 1-bromobutane. |
| (b) 1-chloropropane to butylamine. | (j) Benzene to benzoic acid.  |

- (c) Benzene to 1-phenylethan-1-ol.      (k) Hexane from 1-bromopropane.  
 (d) But-1-ene from ethene.      (l) 1,2-dibromoethane to ethanol.  
 (e) Iodomethane to ethanoic acid.      (m) 2-bromobutane to butanone.  
 (f) Chlorobenzene can be converted into cyclohexene.  
 (g) Chlorobenzene can be converted into cyclohexanol.  
 (h) Ethene to phenol.
- 2-bromo-2-methylpropane reacts with hot water to form 2-methylpropan-2-ol.
    - Write the rate equation for the reaction.
    - Draw the energy diagram for the reaction that took place.
    - Outline the mechanism for the reaction that took place.
    - State the:
      - rate determining state for the reaction.
      - technique which was used to study the reaction.
  - 1-bromobutane undergoes nucleophilic substitution reaction when heated with aqueous sodium hydroxide solution whereas bromobenzene does not react under similar conditions. Explain this observation.
  - An organic compound **P** contains 35.04% carbon, 6.56% hydrogen and 58.04% bromine.
    - Calculate the empirical formula of **P**.
    - The vapour density of **P** was found to be 68.
      - Determine the molecular formula of **P**.
      - Write the names and structural formulae of all the possible isomers of **P**.
    - When **P** was reacted with sodium hydroxide, a compound, **Q** was formed. When a solution of anhydrous zinc chloride in concentrated hydrochloric acid was added to **Q**, it turned cloudy within 10 minutes.
      - Identify **Q**.
      - Write the mechanism for the reaction between **P** and sodium hydroxide and state the condition(s) for the reaction to take place.
    - Explain the difference in the reactivity of **P** and bromobenzene with sodium hydroxide.
    - Write equation(s) to show how **P** can be synthesised from butan-1-ol.
    - 2-bromobutane was treated with sodium ethoxide in ethanol to compound **T**. Write the equation and a mechanism for the reaction between 2-bromobutane and ethoxide in ethanol.
      - The compound, **T** formed in (a) can be synthesised from an alcohol. Write the equation and include a mechanism for the reaction leading to the formation of **T** from an alcohol.

6. (a) Discuss the reactions of bromoethane with potassium hydroxide.  
[Include mechanisms for the reactions].
- (b) (i) Briefly describe a test that can be carried out to distinguish between bromoethane and bromobenzene.
- (ii) Account for the difference(s) in reactivity of bromoethane and bromobenzene.
- (c) Write equation to show how:
  - (i) bromoethane can be prepared from ethanol.
  - (ii) bromobenzene can be prepared from benzene.
- (d) Write the mechanism for the reaction in (c)(ii) above.
7. Compound **Q**,  $C_7H_7Cl$  burns with a sooty flame.
  - (a) Write the structural formulae of all the possible isomers of **Q**.
  - (b) When **Q** was heated with aqueous sodium hydroxide, a primary alcohol, **Z** was formed.
    - (i) Identify **Q**.
    - (ii) Write equation and outline a mechanism for the reaction between **Q** and sodium hydroxide.
  - (c) Write equation to show how **Q** can be converted to 2-phenylethanol.
8. Compound **X**,  $C_8H_9Br$  burns with a sooty flame.
  - (a) Write the structural formulae of all the possible isomers of **X**.
  - (b) When **X** was heated under reflux with aqueous sodium hydroxide, a primary alcohol, **Q**,  $C_8H_{10}O$  was formed.
    - (i) Identify **Q** and **X**.
    - (ii) Write an equation and outline a mechanism for the reaction leading to the formation of **Q** from **X**.
  - (c) **Q** was converted in a one-step reaction to an alkene. Write equation and outline a mechanism for the reaction.
  - (d) The alkene in (c) was polymerised. Write the structural formulae of the polymer.
  - (e) State
    - (i) the type of polymerisation involved in (d).
    - (ii) one used of the polymer formed in (d).
9. Name one reagent that can be used to distinguish between the following pairs of compounds. In each case, state what would be observed if each member of the pair is separately treated with the reagent you have named.

- (a)  and 
- (b)  and 
- (c)  and  $\text{CH}_3\text{CH}_2\text{CH}_2\text{Cl}$
- (d)  and  $\text{H}_3\text{C}-\text{C}_6\text{H}_4-\text{I}$
- (e)  $\text{C}_6\text{H}_5\text{I}$  and  $\text{C}_6\text{H}_5\text{CH}_2\text{I}$
- (f)  and 

10. The structural formula of a compound X is shown below.



When 2.49 g of X was heated under reflux with 24.90 cm<sup>3</sup> of 1.0 M sodium hydroxide solution and the mixture cooled, the resultant cooled mixture required 1.0 M dilute sulphuric acid for complete reaction using phenolphthalein indicator.

- (a) Write equation for the reaction between
- X and sodium hydroxide solution.
  - dilute sulphuric acid and the resultant cooled mixture.
- (b) Determine the volume of volume of dilute sulphuric acid required for complete reaction with the resultant cooled mixture.
- (c) Outline the mechanism for the reaction in (a).