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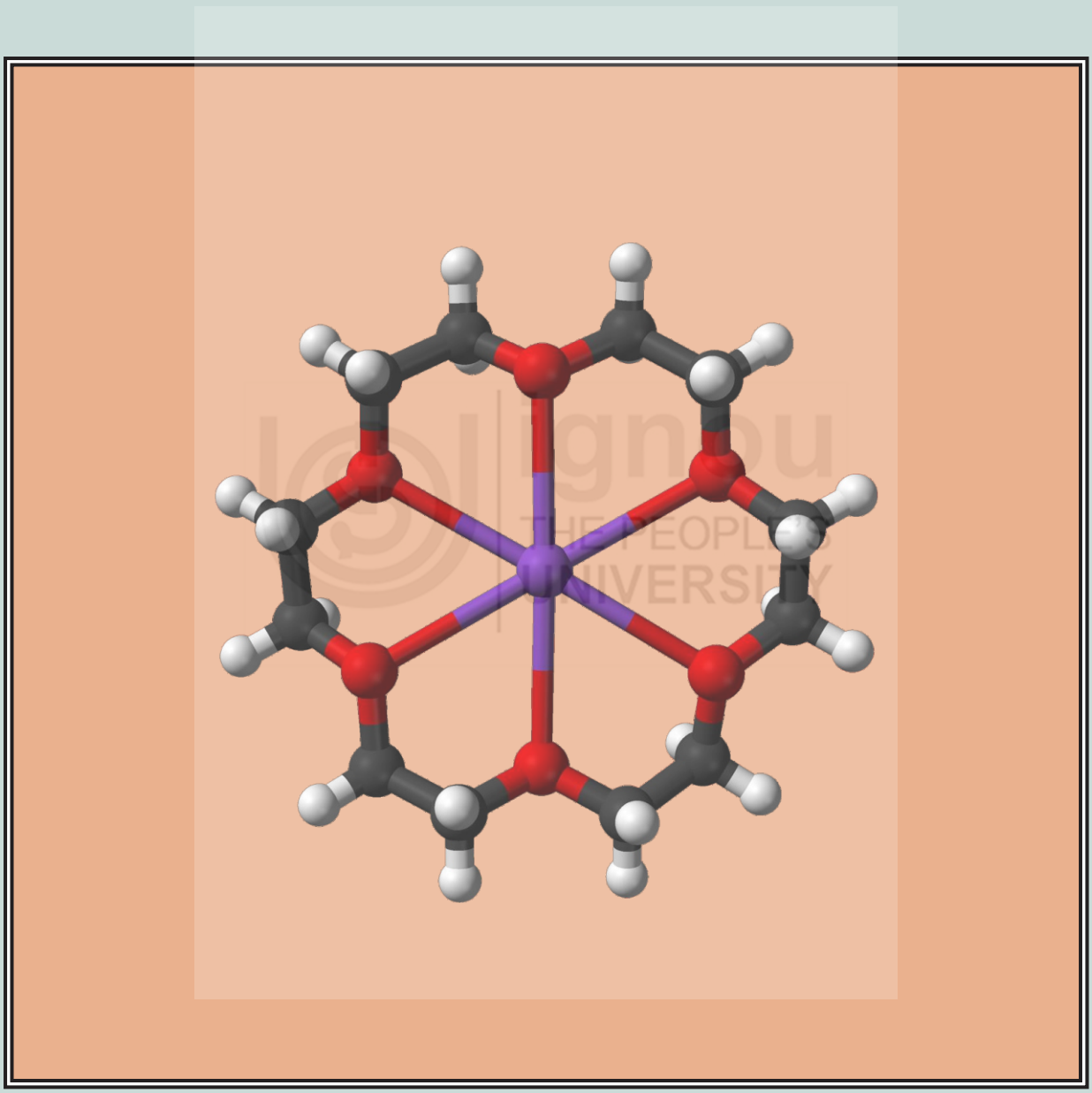
CHEMICAL ENERGETICS, EQUILIBRIA AND FUNCTIONAL ORGANIC CHEMISTRY-I



FUNCTIONAL GROUP ORGANIC CHEMISTRY-I

Vol. 2

''शिक्षा मानव को बन्धनों से मुक्त करती है और आज के युग में तो यह लोकतन्त्र की भावना का आधार भी है। जन्म तथा अन्य कारणों से उत्पन्न जाति एवं वर्गगत विषमताओं को दूर करते हुए मनुष्य को इन सबसे ऊपर उठाती है।''

– इन्दिरा गाँधी

''Education is a liberating force, and in our age it is also a democratising force, cutting across the barriers of caste and class, smoothing out inequalities imposed by birth and other circumstances.''

– Indira Gandhi

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VOL.

2

FUNCTIONAL GROUP ORGANIC CHEMISTRY-I

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Block

3

AROMATIC HYDROCARBONS AND HALOGEN DERIVATIVES

AROMATIC HYDROCARBONS AND HALOGEN DERIVATIVES

In the first course of first semester, we introduced you to the basic concepts of organic chemistry. In that course you learnt about the aliphatic hydrocarbon compounds mainly. A brief description about aromaticity in terms of experimental and theoretical criteria was also dealt in the last unit of that course.

This block contains five units. In Unit 10, 11 and 12 deal with the aromatic hydrocarbons. In these units you will study the preparations and properties of benzene. We shall see the characteristic reactions of aromatic hydrocarbons involve electrophilic substitution reactions, in which the resonance-stabillised ring system is preserved. In the Unit 12, we shall also take up the effect of substituents on the reactivity and the orientation in the benzene ring.

Unit 13 and Unit 14 deal with the chemistry of the halogen derivatives. In Unit 11, our main focus is on the chemistry of alkyl halides. Some important reactions of alkyl halides such as nucleophilic substitutions (S_N1 and S_N2) and elimination reactions (E1 and E2) will be dealt in detail. In Unit 14 we shall take up the unique chemistry of aryl halides. This unit ends with the description on the relative reactivity and relative strength of C—X bond in different type of halogen derivatives.

Expected Learning Outcomes

After studying this block, you should able to:

- describe the preparations of benzene;
- discuss the important reactions of benzene;
- explain the effect of substituents on the reactivity and orientation in benzene ring;
- classify and draw structures of simple halogen derivatives;
- outline the methods of preparation of aliphatic and aromatic halogen derivatives;
- describe reactions of aliphatic and aromatic halogen derivatives;
- explain the mechanism of nucleophilic substitution and elimination reactions of alkyl halides; and
- explain the mechanism of nucleophilic substitution reactions of aryl halides.

UNIT 10

PREPARATION OF AROMATIC HYDROCARBONS

Structure

10.1 INTRODUCTION

Aromatic compounds are the backbone of organic chemistry. Many of the drugs contain aromatic compounds. So it is very important to understand the chemistry of aromatic compounds. Benzene is a basic aromatic hydrocarbon with general formula C_6H_6, having conjugated double bonds. Lots of household items like paints, varnish, detergents etc. contain aromatic compounds.

This is the first Unit of this block. In this unit first we will give you a brief introduction of aromatic compounds. Then we will discuss the isolation and occurrence of benzene. We will recall Huckel's rule for aromaticity. We will also learn the physical properties of benzene. In the last section of this unit, we will discuss different methods for the preparation of benzene and alkyl benzenes.

In the next two units we will familiarise you with the reactions of benzene and alkylbenzenes.

Expected Learning Outcomes

After studying this unit you should be able to:

- explain the basic concept of aromatic hydrocarbons;
- explain Huckel's rule;
- describe the structure of benzene;
- describe the physical properties of benzene;
- describe the carcinogenic nature of benzene; and
- Outline the methods of preparation of benzene and alkylbenzene.

10.2 AROMATIC HYDROCARBONS – AN INTRODUCTION

You have already studied the basics of aromatic compounds in Unit 19 of 1st semester course. The word "benzene" derives from "gum benzoin" (benzoin resin), an aromatic resin. In the earlier stages, the organic compounds were arbitrarily classified as aliphatic or aromatic. The meaning of word "aliphatic" means fatty. The aliphatic compounds were so named because the fatty acids were one of the first members of this class. In addition to the aliphatic compounds, there was a large number of another type of compounds, which were also obtained from natural sources, e.g., resins, balsams, aromatic oils, etc. The structures of these compounds were as unknown but they had one thing in common, a pleasant odour. Thus, these compounds were arbitrarily classified as aromatic compounds (Greek: **aroma** 'fragrant smell'). There was a time when chemists used to smell the compound and sometimes even taste it to identify chemicals. Just because of this wrong practice, a famous Swedish Scientist **Carl Scheele** died while tasting a chemical substance in his laboratory. Another chemist **"Robert Bunsen**" used to tast poisonous arsenic and this made his tongue black.

In present scenario, word aromatic is used for benzene and its derivatives. Remember it does not mean that all the aromatic compounds contain benzene ring. There are number of aromatic compounds which do not contain benzene ring. These types of compounds are classified as **non-benzenoid** aromatic compounds. So we can say that aromatic compounds are of two types:

i) **benzenoid** compounds; and

ii) **non-benzenoid** compounds.

Before we proceed further, let us recall some important facts of aromatic compounds, which will help you to understand this unit. Benzene is a basic aromatic hydrocarbon with the chemical formula C_6H_6. Aromatic hydrocarbons

are compounds having alternate single and double bonds between the two carbon atoms of the ring.

A hydrocarbon can be an aromatic compound if it follows the Huckel's rule. Details of this rule you have studied in Unit 19 of the 1st Semester Course. Let us recall Huckel's rule.

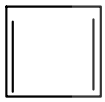
10.2.1 Huckle's Rule

According to Hückel's Rule, a compound can be aromatic if it contains the following distinct properties:

- The compound is a cyclic structure.
- The compound must contain $(4n + 2)\ \pi$ electrons, where n is any number i.e. 1,2,3,4…….. This means that only the rings with 2, 6, 10, 14,……π electrons may be aromatic.
- The compound must be co- planar.

Some examples of the compounds following Huckel's rule are given below:

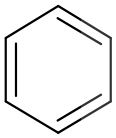
Cyclobutadiene



No. of π-electrons = 4

$4n + 2\pi$-electrons are required for aromacity. Cyclobutadiene has 4 π-electrons, hence cyclobutadiene is not aromatic as it does not follows Huckel's rule.

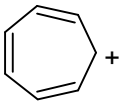
Benzene



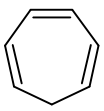
No. of π-electrons = 6

Benzene is a typical example of an aromatic compound. Here, the Huckel's rule is followed as it has 6π electrons which are required for a compound to be aromatic. All the carbon atoms of benzene ring are sp^2 hybridised and it is a planar molecule. It is an excellent example of an aromatic system.

Cycloheptatrienyl cation and cycloheptatriene



1,3,5-cycloheptatrienyl cation



1,3,5-cycloheptatriene

In the above two compounds both have 6π elections but 1, 3, 5-cycloheptatrienyl cation is aromatic and 1,3,5-cycloheptatriene is not. You

can ask why it is so. Cycloheptatriene has three double bonds i.e. 6π electrons but because of the presence of one sp^3 carbon atom it is not coplanar and hence not aromatic compound. In case of cycloheptatrienyl cation generation of the cation removes the hindrance and the delocalised 6π electrons (Huckel's rule) make the cation planar and aromatic.

From the above example, it is clear that a flat planar geometry is required for proper overlap resulting in delocalisation of π-electrons which is a necessary condition for a compound to be aromatic.

SAQ 1

1, 3, 5-cycloheptatrienyl cation is aromatic and 1,3,5-cycloheptatriene is not. Explain.

10.3 OCCURANCE

First time in 1825, Michael Faraday isolated benzene from whale oil giving it the name *bicarburet of hydrogen*. In 1833, a famous scientist Eilhard Mitscherlich obtained benzene by distilling benzoic acid and lime. He gave the compound the name *benzin*.

The biggest consumer country of benzene was China, followed by the USA. Benzene production is currently expanding in the Middle East and in Africa, whereas production capacities in Western Europe and North America are stagnating.

Benzene is produced naturally by volcanoes. In the year 1845, Holman isolated benzene and its derivatives from coal tar. Later on benzene became very important compound in organic chemistry as a large number of the medicines are aromatic in nature, e.g., aspirin, paracetamol, diclofinac sodium, etc.

Benzene is a natural constituent of crude oil and is one of the elementary petrochemicals. Benzene is a byproduct of the incomplete combustion of many materials. In earlier days benzene was obtained as a by-product of coke for the steel industry. After 1950s, the demand of benzene increased tremendously especially for the growing polymer industries, Today, major amount of benzene comes from the petrochemical industries, and only a small fraction is obtained from coal.

SAQ 2

Fill in the following blanks

i) In 1825, Michael Faraday isolated benzene from ----------.

ii) *Benzin* was isolated from ---------- and lime.

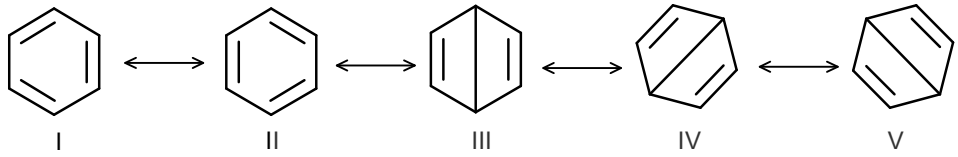
iii) In 1845, Holman isolated benzene and its derivatives from ----------.

iv) ---------- is a byproduct of the incomplete combustion of many materials.

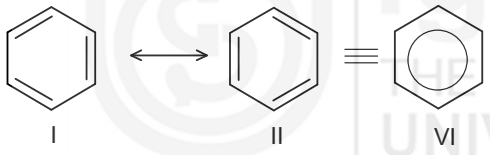
v) Today, major amount of benzene comes from ----------.

10.4 STRUCTURE OF BENZENE

You have studied structure of benzene in Unit 19 of1st semester course. Here we will just recall only important points which will help you to understand this unit. We cannot write a single structure for benzene which would encompass all its properties rather it is considered to be the resonance "hybrid" of the following hypothetical structures I-V:



These structures are called resonance structures or contributors or canonical forms. The two "Kekule" forms, I and II, are of lower energy (more stable) than the three "Dewar" forms, III to V. Structures I and II could be expected to "contribute" more to the hybrid than either III, IV or V. Hence, the properties of benzene would be expected to resemble more closely to either I or II than to III, IV or V. Since I and II have the same energy, each would contribute to the hybrid by the same amount. The symbol of resonance, double-headed arrow (↔), does not indicate an equilibrium. The canonical structures I-V are hypothetical and do not have any physical existence. Structures I and II can be represented as structure VI. It shows that hydrogen atom is attached to each angle of benzene ring.



Orbital picture of benzene

Benzene is visualised as a symmetrical, flat, planar molecule having a regular hexagonal shape. Each carbon atom is bonded to two other carbon atoms and one hydrogen atom by sigma bonds using sp^2 hybrid orbitals, Fig. 10.1 (a). All the carbon-carbon bonds are of equal length of 139 pm, similarly all the carbon-hydrogen bond are of 110 pm. You will notice that all the bond angles of carbon-carbon and carbon-hydrogen atoms are equal i.e.120°.

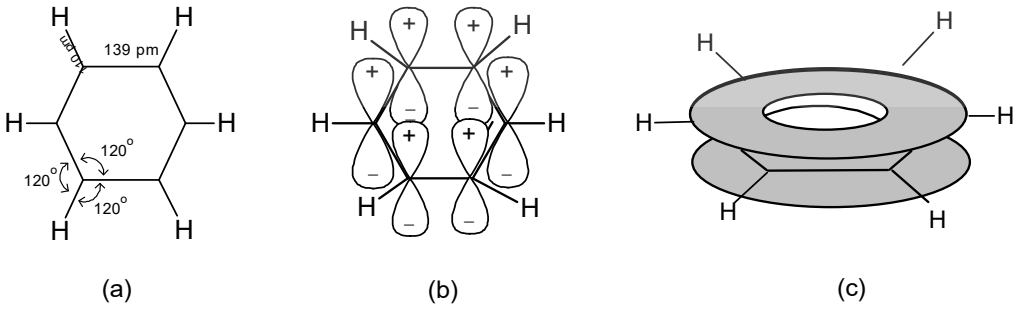


Fig. 10.1: a) σ Skeleton of benzene; b) π Bond formation in benzene; c) π Cloud in benzene, aromatic sexlet.

The third *p* orbital of each carbon atom lies perpendicular to the plane of the molecule and has a lobe each, above and below the plane, as shown in Fig. 10.1 (b). These *p* orbitals have one electron each. The sideways overlap of

these *p* orbitals accounts for the π bonding in benzene. The six electrons which form an electron cloud above and below the plane of the ring are called aromatic sextet, Fig. 10.1 (c).

SAQ 3

Draw the orbital picture of benzene.

10.5 PHYSICAL PROPERTIES OF BENZENE

Aromatic Hydrocarbons are well known for their exceptional physical and chemical properties. In this section we will learn about some important physical properties of benzene.

Octane number is a measure of quality of gasoline: higher the octane number, better the fuel.

Benzene is a colorless liquid at room temperature. It is highly flammable liquid which gives sooty yellow flame on heating. Benzene has sweet smell, which is responsible for the aroma around petrol stations. As benzene has a high octane number, it is an important component of gasoline.

Like other hydrocarbons, benzene is also non-polar in nature. Benzene is immiscible with water and miscible in organic solvents, such as acetone, aldehydes, ethers, carbon tetrachloride, chloroform and hexane etc. Benzene has been widely used as a solvent, but due to its carcinogenic nature it has been banned in most of the countries. Benzene is used to prepare azeotrope with water. Benzene is lighter than water and its density is 0.87g cm^{-3}. Boiling point of benzene is 358.5 K (80.5 ^{o}C) and melting point is 283.5 K (5.5 ^{o}C). Benzene evaporates into the air very quickly. Its vapors are heavier than air and may sink into low-lying areas.

10.6 USES OF BENZENE AND ITS DERIVATIVES

Azeotrope is a **mixture** of liquids that has a constant boiling. The boiling point of an **azeotropic mixture** may be higher or lower than that of any of its components.

Because of the pleasant smell of benzene, in the 19th century benzene was used as an after-shave lotion but due to its carcinogenic nature it was replaced by methylbenzene, which has similar physical properties but it was not carcinogenic. You will be surprised to know that lot of household items contain benzene. Some of them are:

- Paint,
- lacquer,
- varnish removers,
- glues,
- furniture wax,
- detergents and
- thinners.

In several chemical industries, aromatic hydrocarbons have wide applications. Benzene is used mainly as an intermediate to make other chemicals like: ethylbenzene, cumene, cyclohexane, nitrobenzene, and alkylbenzenes. More than half of the entire benzene production is used for the preparation of

ethylbenzene, a precursor to styrene, benzene is used to make plastics, resins, synthetic fibers, rubber lubricants, dyes, detergents, drugs and pesticides.

Due to carcinogenic nature of benzene, in most of the industries, it is being replaced by toluene as a substitute for benzene as a fuel additive.

SAQ 4

Which of the following are true or false? Write "T" for true and "F" for false in the boxes given below

i) Benzene is a colorless or light yellow liquid at room temperature. ☐

ii) Benzene has a low octane number. ☐

iii) Benzene is polar compound. ☐

iv) Benzene is immiscible with acetone. ☐

v) Benzene is used to prepare azeotrope with water. ☐

vi) Benzene is lighter than water. ☐

10.7 CARCINOGENIC NATURE OF BENZENE

As benzene is a carcinogen, most non-industrial applications have been limited. Both International Agency for Research on Cancer (IARC) and Environmental Protection Agency (EPA) declared benzene as "carcinogenic compound". It causes Acute Myeloid Leukemia (AML).

IARC: The International Agency for Research on Cancer is part of the World Health Organization (WHO). One of its goals is to identify causes of cancer.

The major effect of benzene from long-term exposure is on the blood (Long-term exposure means exposure of a year or more). Benzene causes harmful effects on the bone marrow and can cause a decrease in red blood cells, leading to anemia. Benzene oxidises in the body to produce an epoxide, which itself is carcinogenic. The epoxide interacts with DNA to produce cancer.

EPA: Environmental Protection Agency is an agency of the United States federal government whose mission is to protect human and environmental health.

Direct exposure of the eyes, skin, or lungs to benzene can cause tissue injury and irritation. Even death is possible if a person inhales very high levels of benzene. Inhalation of benzene may develop the following symptoms:

- Vomiting,
- Irritation of the stomach,
- Sleepiness,
- Drowsiness,
- Regular heartbeat.,
- Headaches,
- Tremors,
- Unconsciousness.

AML: (**Acute Myeloid Leukemia)** is a cancer of the blood and bone marrow. This type of cancer usually gets worse quickly if it is not treated.

Benzene can react with other air pollutants to form ground levels ozone which can damage crops and other materials.

SAQ 5

What are the symptoms of benzene Inhalation?

10.8 PREPARATION OF BENZENE AND ALKYLBENZENES

Benzene and alkylbenzenes can be prepared by numerous methods. In this unit we will discuss only few of them.

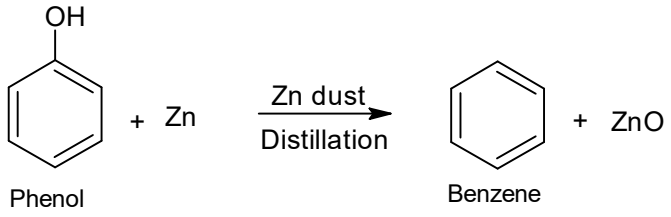
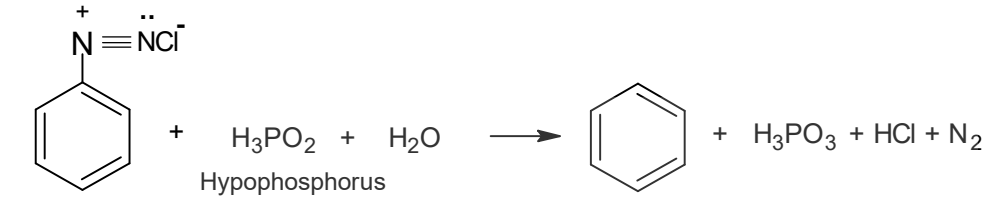
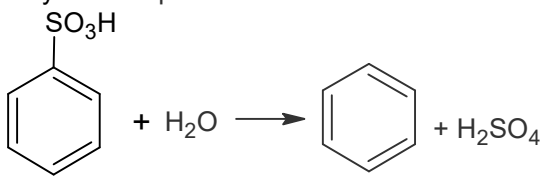
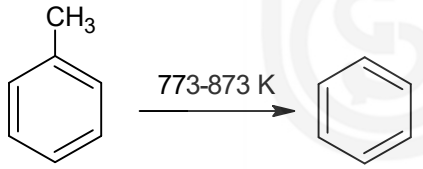
10.8.1 Preparation of Benzene

Benzene can be prepared from aromatisation of aliphatic hydrocarbons, cyclic polymerisation of ethyne, decarboxylation of sodium benzoate, reduction of phenol, hydrolysis of sulphonic acids and reduction of benzenediazonium salts.

Some important methods for preparation of benzene are summarised in Table 10.2.

Table 10.2: Methods of preparation benzene

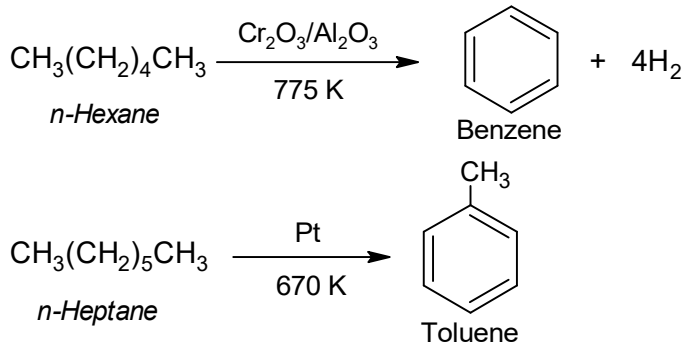
Sr. No.	Reactions
1.	Aromatisation of aliphatic hydrocarbons
	i) $CH_3(CH_2)_4CH_3 \xrightarrow[\text{catalyst}]{\Delta}$ Benzene (*n*-Hexane)
	ii) $CH_3(CH_2)_5CH_3 \xrightarrow[\text{catalyst}]{\Delta}$ Toluene (*n*-Heptane)
	iii) $CH_3(CH_2)_6CH_3 \xrightarrow[\text{catalyst}]{\Delta}$ Xylenes (*n*-Octane)
2.	Cyclic polymerisation of ethyne $3\ HC{\equiv}CH \xrightarrow[300^{\circ}C]{Cu}$ Benzene Acetylene
3.	Decarboxylation of sodium benzoate Sodium benzoate + $NaOH \xrightarrow{CaO}$ Benzene + Na_2CO_3

4.	Reduction of phenol  Phenol Benzene
5.	Reduction of Benzenediazonium Salts  Benzene diazonium chloride Hypophosphorus acid Benzene
6.	Hydrolysis of sulphonic acids:  Sulphonic acid Benzene
7.	Hydrodealkylation  Toluene Benzene

Let us study each method in detail.

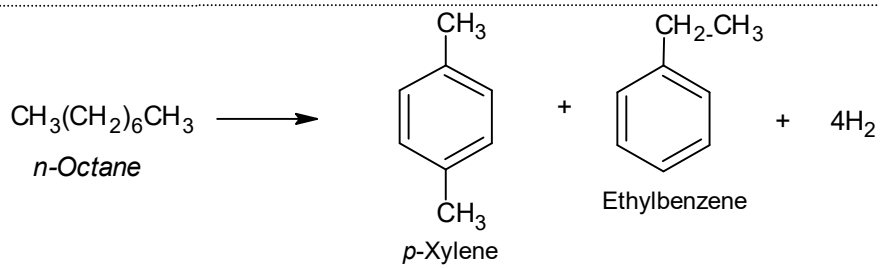
i) Aromatization of aliphatic hydrocarbons or Hydroforming

This is a process of converting aliphatic hydrocarbon to aromatic hydrocarbons. This is also known as **hydroforming or catalytic reforming.** Alkane with six or more carbon atoms, when heated strongly (775 K) under pressure in the presence of platinum catalyst, gives aromatic hydrocarbon. This process involves cyclisation, isomerisation and dehydrogenation. In this process, the product contains the same number of carbon atoms as the aliphatic starting materials. Aromatization of gasoline increases their octane number from 40 to 95 because unsaturated hydrocarbons are better fuels.



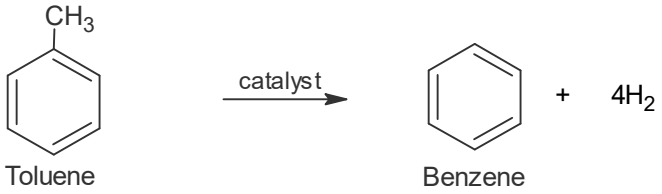
n-Hexane Benzene

n-Heptane Toluene



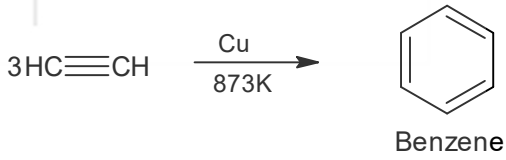
Catalytic aromatisation in the presence of platinum is sometimes referred to as platforming or hydroforming. This process also constitutes a valuable method for commercial production of these hydrocarbons.

Since, benzene is obtained in much smaller amount than toluene can be converted into benzene by heating with hydrogen under pressure in the presence of a metal oxide catalyst. This process is called **hydro-dealkylation.**

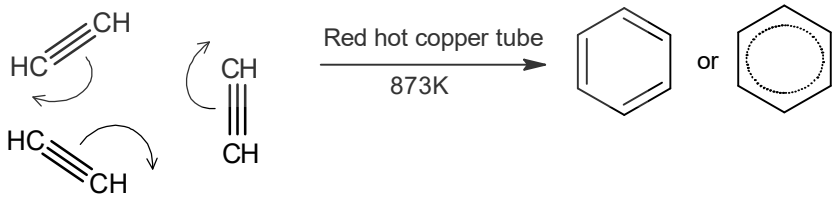


ii) Cyclic Polymerisation of Ethyne

Ethyne undergo two types of polymerisation reaction- i) linear and ii) cyclic. Cyclic polymerization of ethyne results in the formation of aromatic hydrocarbons. It is one of the important chemical reactions of alkynes. When ethyne (acetylene) gas is passed through a red hot copper tube at 873 K, the ethyne molecules then undergo cyclic polymerization to form benzene.

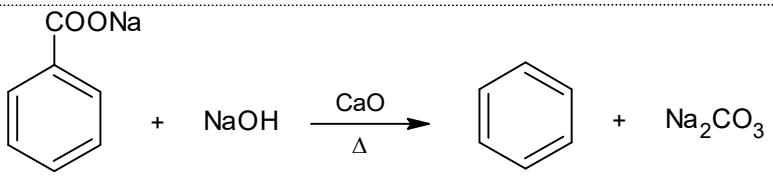


Here copper acts as catalyst. Three molecules of ethyne are involved in this reaction. This can be explained from following mechanism.



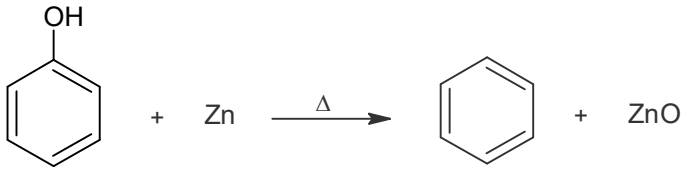
iii) Decarboxylation of sodium benzoate

Benzene can be prepared from aromatic acids. Decarboxylation of sodium benzoate gives benzene. Reaction of sodium salt of the benzoic acid (sodium benzoate) with sodium hydroxide in presence of calcium hydroxide (mixture of sodium hydroxide and calcium hydroxide is known as soda lime) gives benzene and sodium carbonate. This is a common method of preparation of benzene in laboratory. For example:



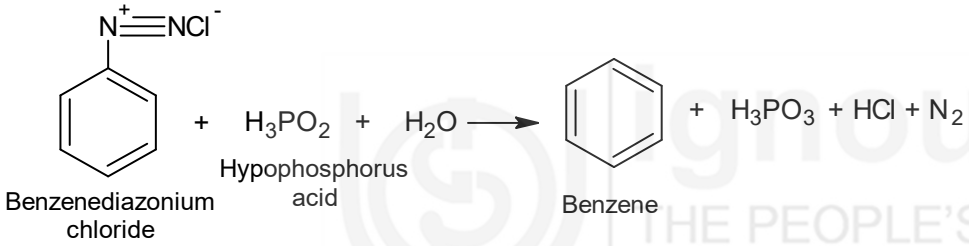
iv) Reduction of phenol

Benzene can be prepared by reduction of phenol. When phenol vapours are passed over heated zinc dust, benzene is formed. This reaction takes place in presence of strong reducing agents like zinc with strong heating.



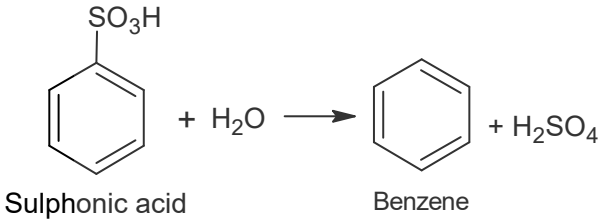
v) Reduction of Benzenediazonium Salts

Benzene can be prepared from benzenediazonium salts by heating it. Reduction of benzenediazonium chloride with hypophosphorus acid yields benzene.



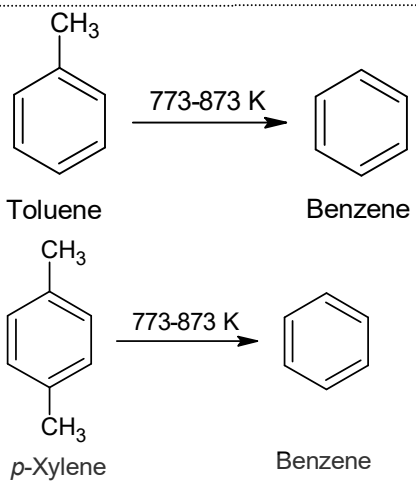
vi) Hydrolysis of sulphonic acid

Benzene can be prepared by hydrolysis of sulphonic acids. In this reaction, sulphonic acid is exposed to superheated steam leading to the formation of benzene.



vii) Hydrodealkylation of Toluene

Toluene can be converted into benzene by dealkylation. In this reaction toluene and hydrogen is heated at a high temperature (773-873 k) and 40–60 atm pressure, in presence of a catalyst chromium, molybdenum, or platinum oxide . Sometimes, much higher temperatures are used instead of a catalyst (at the similar reaction condition). Under these conditions, toluene undergoes dealkylation to benzene and methane. This reaction gives good yield benzene i.e. about 95. Xylenes can also be converted into benzene with similar efficiency.

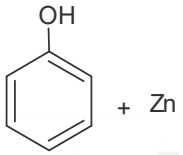


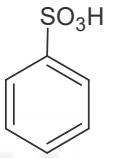
SAQ 6

Predict the products of the following reactions:

i) $CH_3(CH_2)_4CH_3 \xrightarrow{\Delta}$ Hexane

ii) $3\ HC{\equiv}CH \xrightarrow[300^oC]{Cu}$ Acetylene

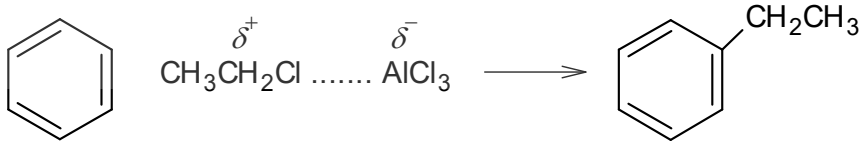
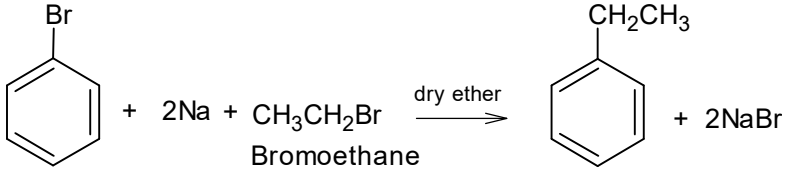
iii)  + Zn $\xrightarrow[\text{Distillation}]{\text{Zn dust}}$ Phenol

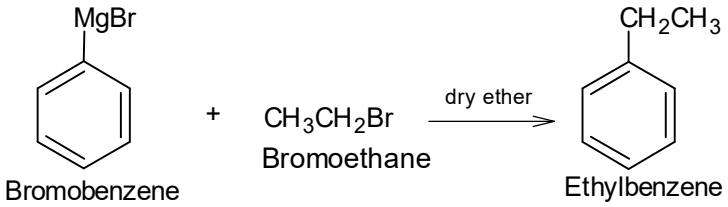
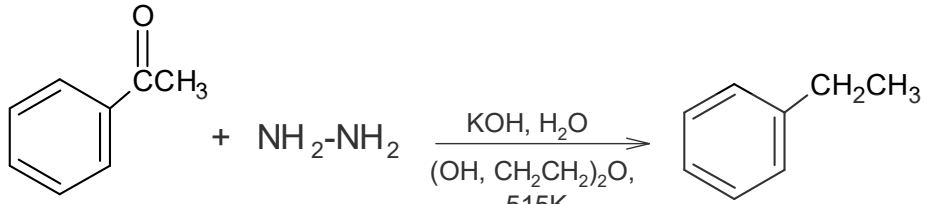
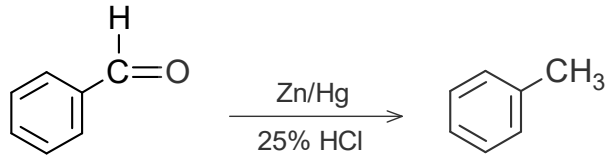
iv)  + $H_2O \longrightarrow$ Sulphonic acid

10.8.2 Preparation of Alkylbenzenes

Alkylbenzenes are very important aromatic compounds. They can be prepared from Friedel-Crafts alkylation, Wurtz-Fittig reaction, Grignard reagent, Wolff-Kishner reduction and Clemmensen reduction. Some important methods for preparation of alkylbenzenes are summarised in Table 10.3.

Table 10.3: Methods of preparation alkylbenzenes (Arenes)

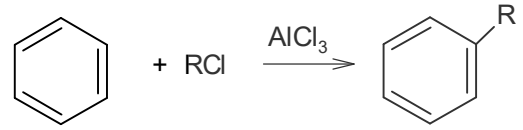
Sr. No.	Reactions
1.	Friedel-Crafts Alkylation  Benzene + CH_3CH_2Cl ..... $AlCl_3$ → Ethylbenzene
2.	Wurtz-Fittig reaction  Bromobenzene + 2Na + CH_3CH_2Br (Bromoethane) $\xrightarrow{\text{dry ether}}$ Ethylbenzene + 2NaBr

3.	From Grignard reagent  Bromobenzene Ethylbenzene
4.	Wolff-Kishner reduction  Acetophenone Ethylbenzene
5.	Clemmensen Reduction  Benzaldehyde Toluene

Now let us discuss each reaction in detail.

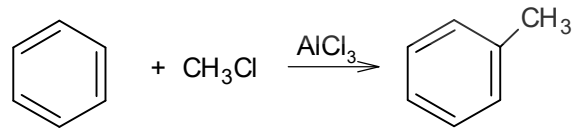
i) Friedel-Crafts Alkylation

Benzene on heating with a haloalkane in the presence of anhydrous aluminum chloride gives its homologue, alkylbenzene. This reaction is known as **Friedel–Crafts reaction.** Details of this reaction you will learn in Unit 11 of this course.

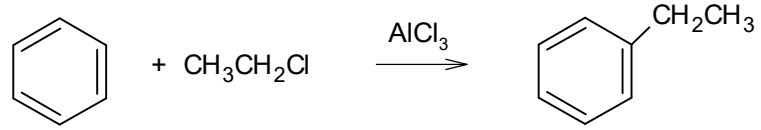


Benzene Alkylbenzene

Benzene on heating with chloromethane gives methylbenzene (toluene) and with chloroethane it gives ethylbenzene.



Benzene Methylbenzene



Benzene Ethylbenzene

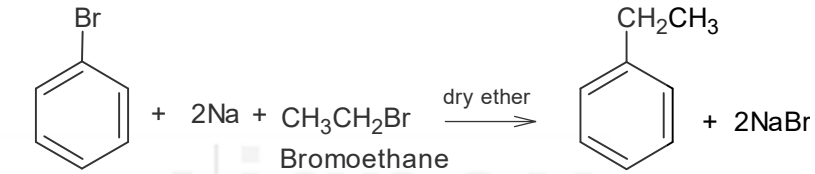
ii) Wurtz–Fittig reaction:

In year 1855, Charles-Adolphe Wurtz reported a reaction what is now known as the Wurtz reaction. In Wurtz reaction, two molecules of alkyl halide are treated with sodium in dry ether to give alkanes. Details of this reaction, you have studied in Unit 15 of 1st semester course

$$2RX + 2Na \longrightarrow RR + 2NaX$$

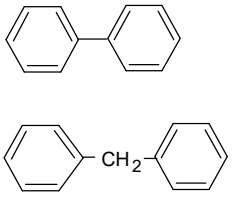
In the 1860s, another scientist Rudolph Fittig extended the Wurtz reaction by coupling of an alkyl halide with an aryl halide. This modification of the Wurtz reaction is considered a separate process and is named for both scientists i.e. **Wurtz–Fittig reaction.**

Alkylbenzenes, also known as Arenes, can be obtained by the reaction aryl halides and alkyl halide. In this reaction aryl halides and alkyl halides are treated with sodium in presence of dry ether. The result is the joining of alkyl and phenyl groups with the loss of halogens. The product is alkyl benzene (Arenes). This reaction is called **Wurtz–Fittig reaction**



Bromobenzene Ethylbenzene

Biphenyl: In isolated systems, two or more rings are joined to each other either directly or through carbon chain.



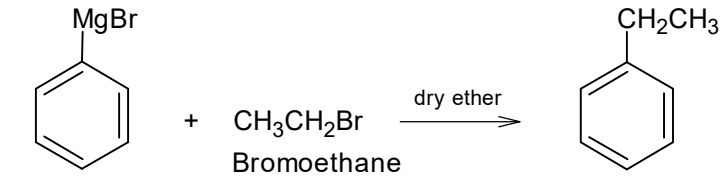
The Wurtz-Fittig reaction can also take place with metals other than sodium, like potassium, iron, copper, and lithium. In presence of lithium, it gives good yield but under ultrasonic irradiation.

The reaction works best for forming asymmetrical products. Typically the reaction is used for the alkylation of aryl halides. However, with the use of ultrasound, the reaction can also be made useful for the production of biphenyl compounds

Like Wurtz reaction, Wurtz-Fittig reaction also gives some undesired side products, which limits its applications.

iii) From Grignard Reagent:

Alkylbenzenes (Arenes) can also be prepared by the reaction of arylmagnesium halide (Grignard reagent) and alkylhalide. For example

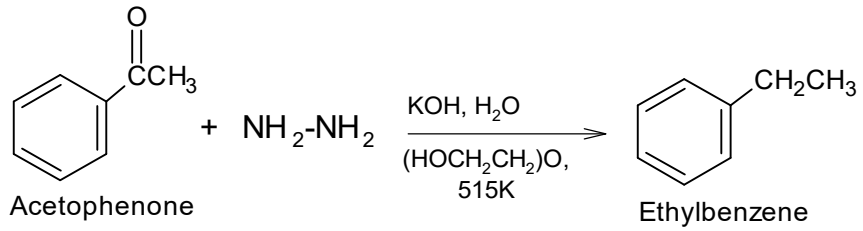


Phenylmagnesium bromide Ethylbenzene

iv) Wolff-Kishner Reduction

Aldehydes and ketones can be reduced to alkanes by treating them with hydrazine, $H_2N - NH_2$, at a high temperature, in alkaline medium. This reaction

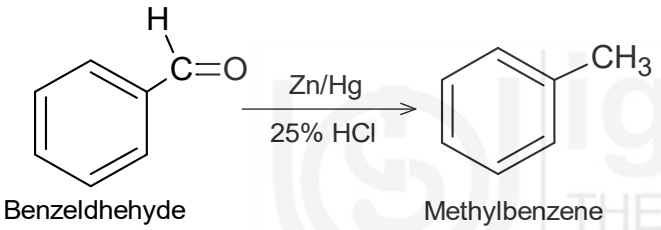
is known as Wolff-Kishner reduction. It is a useful synthetic method for converting an aldehyde or a ketone to an alkane. For example,



Wolff-Kishner reduction can be carried out at room temperature if a strong base like potassium 2-methyl-2-propoxide is used in a polar solvent like dimethyl sulphoxide

v) Clemmensen Reduction

Clemmensen Reduction is used to reduce alkylhalide and ketones this results in the conversion of CO group to CH_2 group. In other words aldehydes and ketones can be converted to the corresponding alkanes under acidic conditions by **Clemmensen reduction**. In this reaction, zinc amalgam (an alloy of zinc and mercury) and concentrated HCl are used to reduce an aldehyde or ketone.



Wolff-Kishner or Clemmensen reduction is particularly useful for the synthesis of compounds having alkyl groups attached to benzene ring. You may recall that Friedel-Crafts alkylation can also be used for this purpose. But in Friedel-Crafts alkylation, rearrangement of the alkyl groups is usually observed.

10.9 SUMMARY

- Benzene is a basic aromatic hydrocarbon with the chemical formula C_6H_6. Aromatic Hydrocarbons are compounds having alternate σ and π bonds between the carbon atoms of the ring.
- A hydrocarbon can be an aromatic compound if it follows the Huckel's Rule and is a planar molecule. According to Huckel's Rule, a compound must contain $(4n + 2)$ π electrons, (where n is any number i.e., 0,1,2,3,4……..) and must be co- planer .
- Benzene is produced naturally by volcanoes. Coal tar is a good source of benzene.
- Benzene is a colorless highly flammable liquid at room temperature.
- Benzene is non-polar solvent which is immiscible with water and miscible in organic solvents. Benzene is lighter than water and its density is 0.87g

cm^{-3}. Boiling point of benzene is 358.5 K (80.5 ^oC) and melting is 283.5 K (5.5 ^oC)

- Lot of household items like paint, lacquer, varnish removers, glues, furniture wax, detergents and thinners contain benzene.
- Benzene can be prepared by:
  - Aromatization of aliphatic hydrocarbons or hydroforming
  - Cyclic Polymerization of ethyne
  - Decarboxylation of sodium benzoate
  - Reduction of phenol
  - Reduction of benzenediazonium Salts
  - Hydrolysis of sulphonic acids
  - Dealkylation of toluene
- Alkylbenzene can be prepared by:
  - Friedel-Crafts alkylation
  - Wurtz–Fittig reaction
  - Grignard reagent
  - Wolff-Kishner reduction
  - Clemmensen reduction

10.10 TERMINAL QUESTIONS

1 What are the main points of Huckel's rule?

2. How would you prepare benzene form ethyne? Give its mechanism

3. What is hydroforming ? Explain with the help of an example.

4 Give one example of the following name reactions

i) Friedel-Crafts Alkylation

ii) Wurtz-Fitting reaction

iii) Clemmensen Reduction

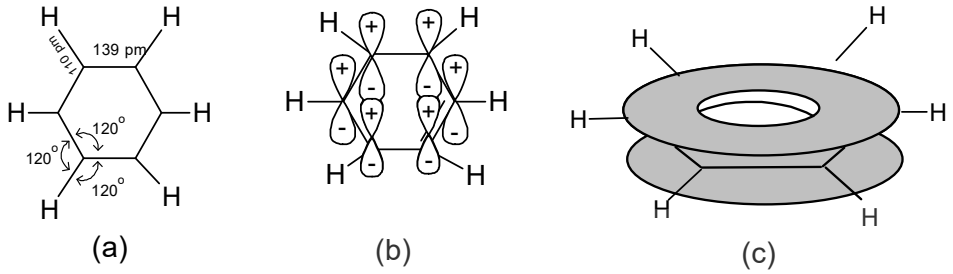
iv) Wolff-Kishner reduction

10.11 ANSWERS

Self-Assessment Questions

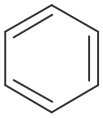
1. Cycloheptatriene has three double bonds i.e. 6π electrons but because of the presence of one sp^3 carbon atom it is not coplanar and hence not aromatic compound. In case of cycloheptatrienyl cation, generation of the cation removes the hindrance and the delocalised 6π electrons (Huckel rule) make the cation planar and aromatic.

2. i) whale oil
   ii) benzoic acid
   iii) coal tar.
   iv) benzene
   v) the petrochemical industries.

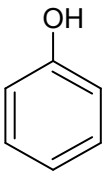
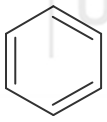
3. 

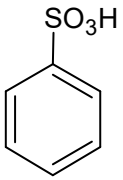
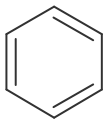
4. i) T , ii) F, iii) F, iv) F, v) T, vi) T

5. Vomiting, irritation of the stomach, sleepiness, drowsiness, irregular heartbeat, headaches, tremors, unconsciousness.

6. i) $CH_3(CH_2)_4CH_3 \xrightarrow{\Delta}$ 
   Hexane — Benzene

   ii) $3\,HC{\equiv}CH \xrightarrow[300^oC]{Cu}$ 
   Acetylene — Benzene

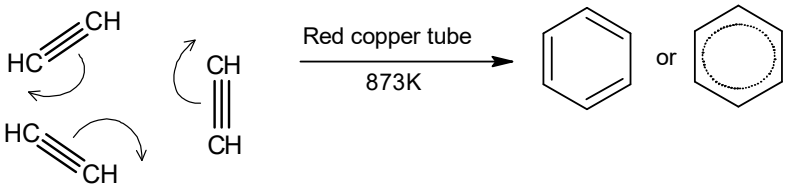
   iii)  $+ Zn \xrightarrow[\text{Distillation}]{\text{Zn dust}}$  $+ ZnO$
   Phenol — Benzene

   iv)  $+ H_2O \longrightarrow$  $+ H_2SO_4$
   Sulphonic acid — Benzene

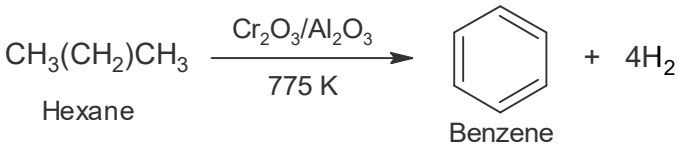
Terminal Questions

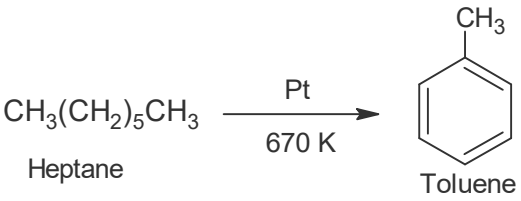
1. The important points of Hückel's rule are:
   - The compound should be a cyclic structure.
   - The compound must contain $(4n + 2)\ \pi$ electrons, where n is any number i.e. 0,1,2,3,4…….. This means that only the ring with 2, 6, 10, 14,……π electrons may be aromatic.
   - The compound must be co- planar.

2. Cyclic polymerisation of ethyne results in the formation of aromatic hydrocarbons. When ethyne (acetylene) gases is passed through a red hot copper tube at 873 K, The ethyne molecules then undergo cyclic polymerization to form benzene.

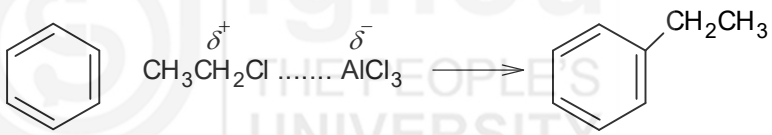


3. This is a process of converting aliphatic hydrocarbon to aromatic hydrocarbons. This is also known as **hydroforming or catalytic reforming.** Alkane with six or more carbon atoms, when heated strongly (775 K) under pressure in the presence of platinum catalyst, gives aromatic hydrocarbon. This process involves cyclisation, isomerisation and dehydrogenation. In this process the product contains the same number of carbon atoms as the aliphatic starting materials.

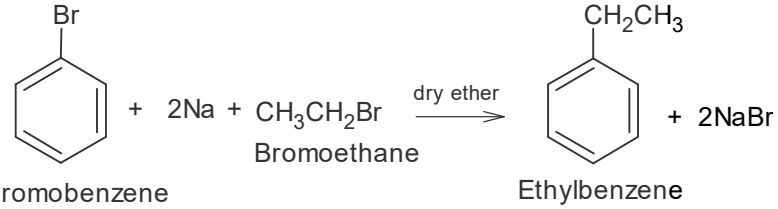




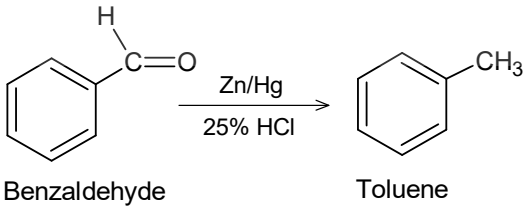
4. i) Friedel-Crafts Alkylation



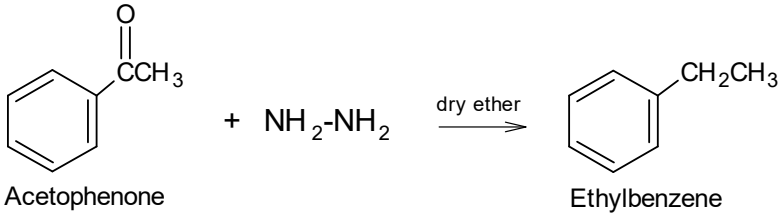
ii) Wurtz-Fittig reaction



iii) Clemmensen Reduction



iv) Wolff-Kishner reduction



UNIT 11

REACTIONS OF AROMATIC COMPOUNDS-I

Structure

11.1 INTRODUCTION

In the previous Unit, we have discussed isolation, preparation of benzene and alkylbenzene. Benzene is the most important aromatic compound. In this unit we will study some important reactions of benzene.

Benzene is carcinogenic and injurious to health. Prolonged exposure to benzene leads to bone-marrow depression. Therefore, benzene should used as a solvent carefully, avoiding evaporation in the open or inhaling its vapours.

Keeping in view the importance of aromatic compounds, we shall study some important electrophilic substitution reactions of benzene like nitration, halogenation and sulphonation in this unit. It is important to understand the pathway of any chemical reaction, so we will discuss the mechanism of these electrophilic substitution reactions. In addition to this, we will discuss Freidel-Crafts alkylation and Freidel-Crafts acylation of aromatic compounds. At the end we will learn some addition reactions, like chlorination and reduction of benzene. In the next unit, we will study reactions of alkylbenzene in detail.

Expected Learning Outcomes

After studying this unit, you should be able to:

- ❖ discuss the nitration, halogenations and sulphonation of benzene;
- ❖ discuss the Friedel-Crafts alkylation of benzene;
- ❖ explain the limitations of Friedel-Crafts alkylation reactions;
- ❖ discuss the Friedel-Crafts acylation of benzene;
- ❖ explain the mechanism of electrophilic substitution reactions of benzene;
- ❖ describe the addition reactions of benzene; and
- ❖ discuss reduction of benzene.

11.2 REACTIONS OF AROMATIC COMPOUNDS

The characteristic reactions of aromatic compounds are electrophilic substitution, in which the resonance-stabilised ring system is preserved. Why is this so? You may answer by saying that this is due to the resonance stabilisation of the benzene. But then the question arises, why then benzene enters into reactions at all, why is it not inert? This dual behaviour, the coexistence of stability and reactivity is due to the presence of the circulating π electrons in the benzene ring which, on one hand, keep the carbon nuclei within bonding distance and, on the other, offer a site of attack to positively charged species i.e. electrophile.

Electrophilic substitution includes a wide variety of reactions, such as nitration, halogenation, sulphonation, Friedel-Crafts alkylation and Freidel-Crafts acylation reactions. Infect, electrophilic substitution reactions undergone by nearly all aromatic rings. In addition to electrophilic substitution reactions, benzene also undergoes few addition reactions. Some important reactions are summarised in Table 11.1.

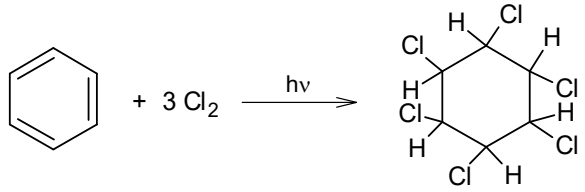
Table 11.1: Reactions of Benzene

1) Nitration $ArH + HNO_3 \xrightarrow{H_2SO_4} ArNO_2 + H_2O$
2) Halogenation $ArH + X_2 \xrightarrow{Fe} ArX + HX$
3) Sulphonation $ArH + SO_3 \xrightarrow{H_2SO_4} ArSO_3H + H_2O$
4) Friedel-Crafts alkylation $ArH + RCl \xrightarrow{AlCl_3} ArR + HCl$

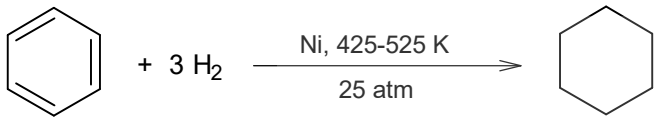
5) Friedel-Crafts acylation

$$ArH + RCOCl \xrightarrow{AlCl_3} ArCOR + HCl$$

6) Addition of halogen to benzene



7) Reduction of benzene



Note: Ar = C_6H_5-

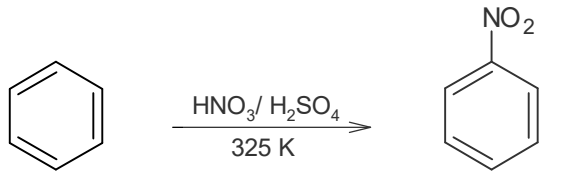
Let us study these reactions in detail.

11.3 ELECTROPHILIC AROMATIC SUBSTITUTION REACTIONS

In this section, we will discuss some important electrophilic substitution reactions of aromatic compounds, taking example of benzene. The characteristic reactions of aromatic compounds are electrophilic substitution reactions. In these reactions electrophile attacks the aromatic π electrons and replaces one hydrogen atom of the aromatic ring. Benzene is a conjugated system with six π elections, hence benzene acts as an electron donor in most of the reactions.

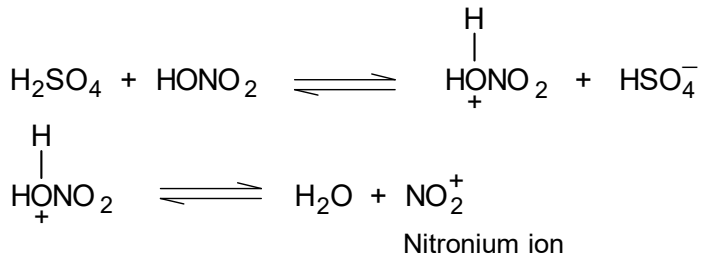
11.3.1 Nitration

Replacement of a hydrogen atom of the aromatic compound in the ring by the nitro-group is known as **"Nitration"**. The nitration of benzene gives nitrobenzene. Nitration of benzene can be carried out by reaction of benzene with a mixture of concentrated nitric and sulphuric acids.



Benzene Nitrobenzene

The electrophile in this reaction is the nitronium ion, NO_2^+. It is generated by the reaction of H_2SO_4 with HNO_3.



Nitronium ion

Further evidence for the participation of the nitronium ion comes from the fact that other species capable of producing nitronium ion, such as $NO_2^+ BF_4^-$, $NO_2^+ NO_3^-$ and $NO_2^+ ClO_4^-$ and also nitrate benzenoid compounds.

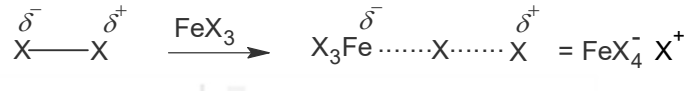
Nitration of benzene is an important reaction because the nitro group can be converted into other functional groups.

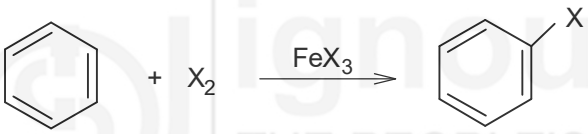
SAQ 1

Give the reaction for generation of NO_2^+.

11.3.2 Halogenation

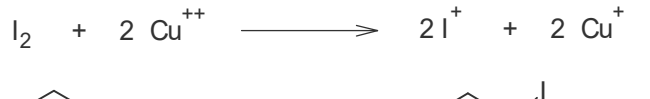
Normally benzene does not react with halogens. Halogens are not electrophilic enough to attack on aromatic ring. However, benzene reacts with halogens in the presence of Lewis acid as catalyst ($FeBr_3$, $FeCl_3$) to yield halogen substituted products, i.e., aryl halides. In presence of a catalyst, halogens become a powerful electrophile. The main function of the catalyst is to partially or completely polarise the halogen-halogen bond and generate X^+ e.g.

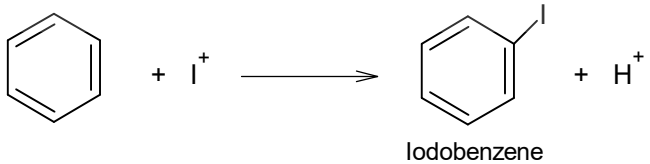




X = Br_2, Cl_2

A typical reaction of aromatic halogenations is the bromination of benzene. As a general rule, fluorine is too reactive and a poor yield of fluorobenzene is obtained. Chlorine reacts smoothly and gives an excellent yield of chlorobenzene. Iodine itself is unreactive; however, iodination of benzene is carried out in the presence of oxidising agent such a hydrogen peroxide, H_2O_2, or copper salt such as $CuCl_2$. This oxidising agent oxidises molecular iodine to an electrophile I^+

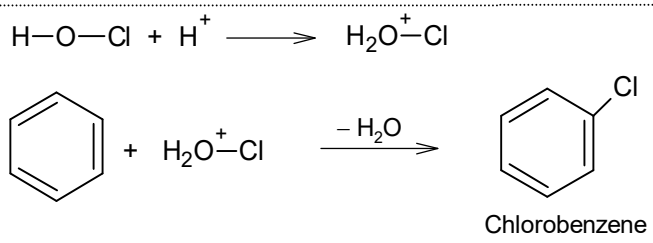




Reactivity of halogens has the following order:

$I_2 < Br_2 < Cl_2$

Halogenations can also be affected by other reagents, such as hypochlorous or hypobromous acids in presence of strong acids.



SAQ 2

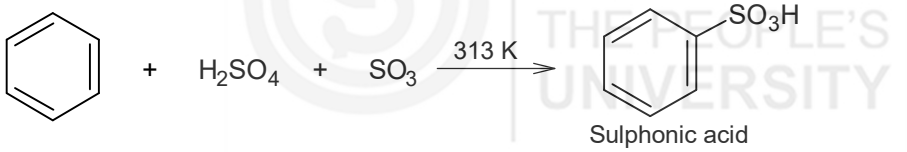
Fill in the following blanks

i) Benzene reacts with halogen in presence of catalyst to produce ……...

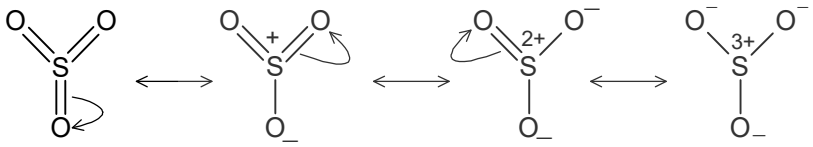
ii) The main function of catalyst is to polarise the ……bond.

11.3.3 Sulphonation

Benzene can be sulphonated by the reaction with fuming sulphuric acid ($H_2SO_4 + SO_3$) Benzene reacts with HSO_3^+ to give benzenesulphonic acid. Aromatic compounds in which the sulphonic group ($– SO_3H$) is directly attached to the benzene ring are called aromatic sulphonic acids. Replacement of hydrogen of benzene by the sulphonic group is called sulphonation. This is another example of electrophilic substitution reaction. Sulphonation is usually accomplished using sulphuric acid or fuming sulphuric acid ($H_2SO_4 + SO_3$) containing varying proportions of sulphur trioxide. This mixture is called "oleum".



Here the reactive spice is neutral SO_3, as is evident from its structure given below:



Unlike other electrophilic substitution reaction of benzene, sulphonation is a highly reversible reaction and the direction depends on the reaction conditions. Sulphonation is favoured in the presence of concentrated or fuming sulphuric acid, however, desulphonation is favoured in hot, dilute aqueous acids. Sulphonation is used in preparation of detergents and manufacture of dyes.

SAQ 3

Fill in the following blanks:

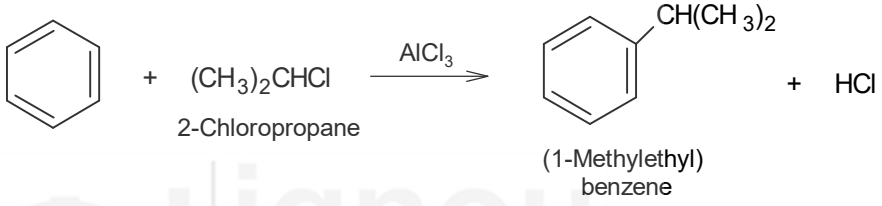
i) Sulphonation is an …….. substitution reaction .

ii) Desulphonation is not possible in …… acid.

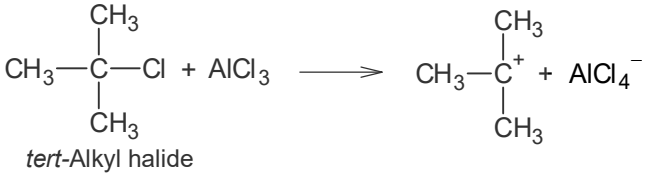
11.3.4 Friedel-Crafts Alkylation

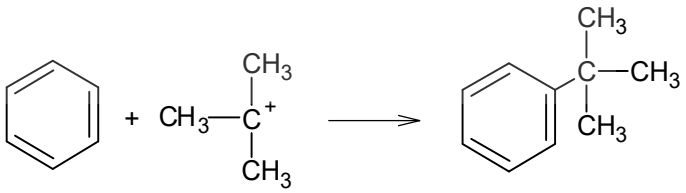
In 1877 two scientists Freidel and Crafts discovered the alkylation of benzene in presence of $AlCl_3$. Introduction of alkyl group in an aromatic ring is called Friedel-Craft alkylation. Complex substituted aromatic compounds are almost always synthesised from the simpler, readily available aromatic compounds. Since benzene is very common and easily available, chemists use it as starting material and introduce the desired substituents. You have already studied the introduction of halogen, nitrogen and sulphur-based functional groups in the aromatic ring. Now you will study another important reaction, i.e., alkylation of aromatic ring.

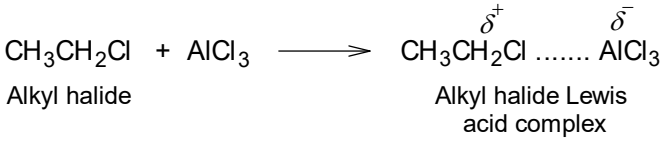
Reaction of benzene with haloalkane in presence of aluminium halide gives alkylbenzene and hydrogen halide. This reaction is known as Friedel-Craft alkylation. Friedel-Craft alkylation can also take place in presence of any other Lewis acid as catalyst. The reaction of 2-chloropropane with benzene in the presence of $AlCl_3$ to yield (1-methylethyl) benzene is a typical Friedel-Crafts alkylation reaction.

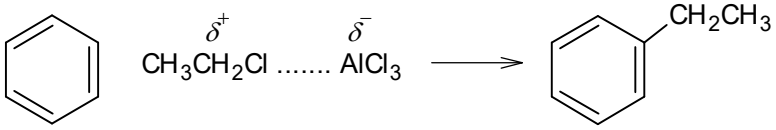


The electrophile in the Friedel-Crafts reaction is R^+. This ion is formed when an alkyl halide reacts with a Lewis acid. Lewis acids, such as $AlCl_3$, $FeCl_3$, $ZnCl_2$, $AlBr_3$, BF_3 etc. are used in Friedel-Crafts alkylations. In case of alkylation with tertiary alkyl halides, the electrophilic species is a free carbocation. However, in primary and secondary alkyl halides, it appears that instead of free carbocations, the electrophilic species is an alkyl halide Lewis acid complex with positively polarised carbon.









The reactivity of haloalkane increases with polarity of C–X bond. The order is:

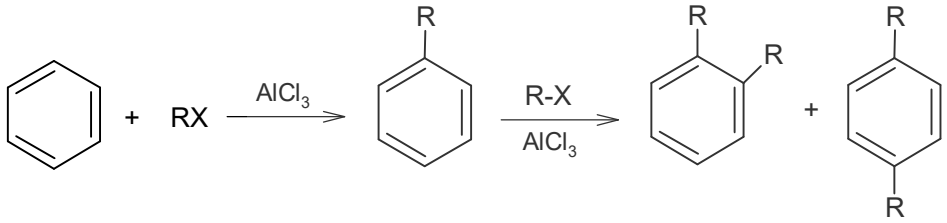
$$RI < RBr < RCl < RF$$

R= Alkyl group

Friedel-Crafts reaction is widely applicable in organic synthesis. However, it has some limitations, which are given below:

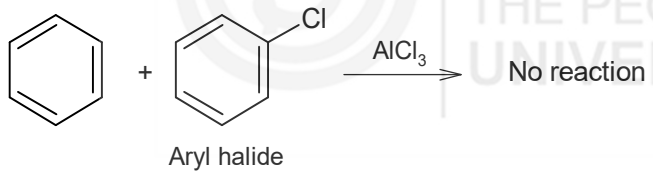
Limitations of Friedel-Crafts Alkylation

i) The main difficulty with the Friedel-Crafts alkylation is that the substitution of the first alkyl group activates the ring towards further substitution.

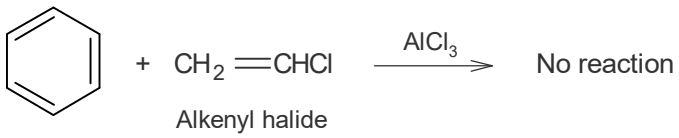


The best way of avoiding this second reaction is to use an excess of aromatic compound.

ii) Friedel-Crafts alkylation reactions are limited to alkyl halides, aryl halides and alkenyl halides do not react. This is because aryl and alkenyl carbocations are too unstable to form under Friedel-Crafts reaction conditions.



Aryl halide

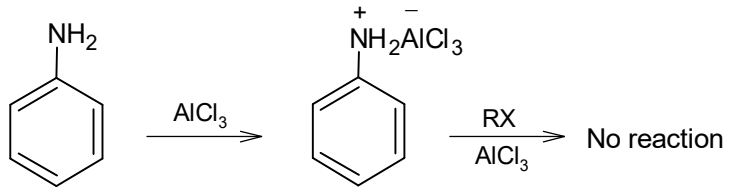


Alkenyl halide

iii) If the aromatic compound has an electron withdrawing substituent, it does not undergo Friedel-Crafts alkylation since the deactivated ring is not reactive to attack by carbocations.

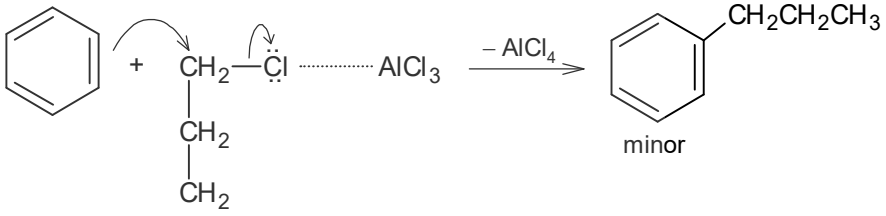
G = electron-withdrawing group

iv) Aromatic amines fail to undergo alkylation, probably because amino group forms a complex with Lewis acid. Since this complex has a positive charge on nitrogen, it deactivates the aromatic ring for electrophilic substitution.

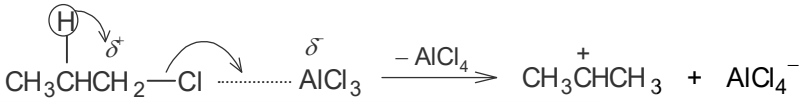


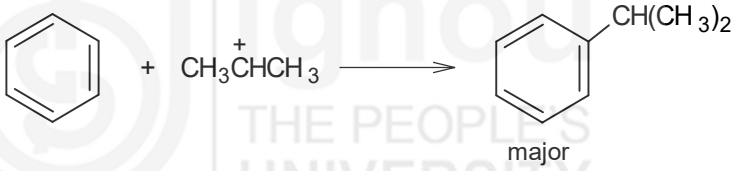
v) Sometimes during the alkylation, the attacking electrophile undergoes rearrangement by 1, 2-shift of H or R. For example, the alkylation of benzene with 1-chloropropane leads to a mixture of *n*-propylbenzene and (1-methyl)ethyl benzene.

No rearrangement



Rearrangement

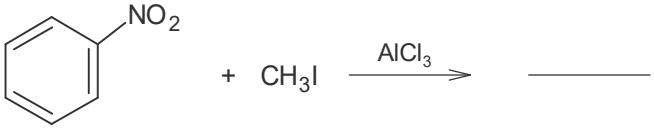


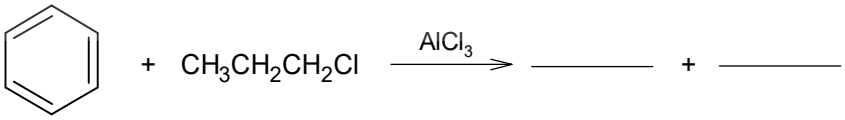


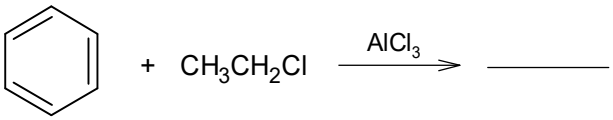
The mechanism is similar to alkylation with an alkyl halide and this reaction proceeds through the more stable carbocation intermediate.

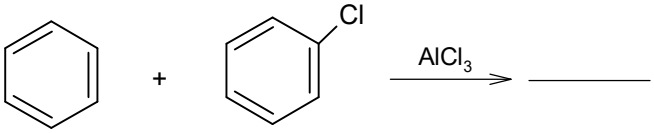
SAQ 4

Give the product(s) of the following reactions:

a) 

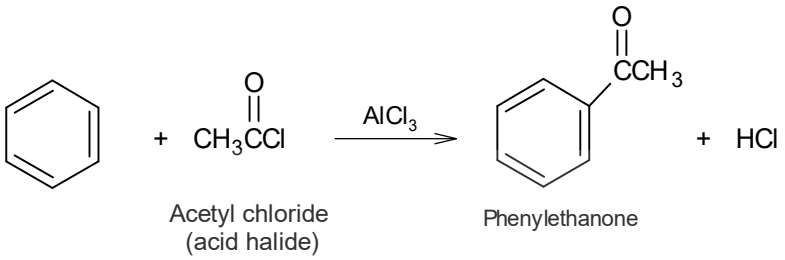
b) 

c) 

d) 

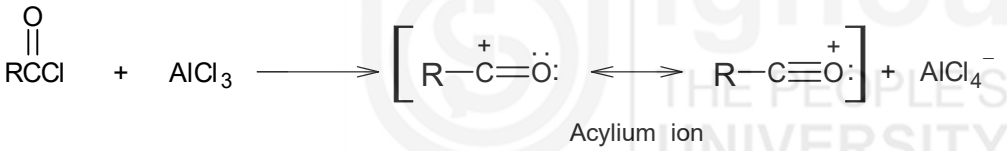
11.3.5 Friedel-Crafts Acylation

The RCO– group or ArCO– group is called an acyl group. Substitution of an acyl group into an aromatic ring by the reaction with an acid chloride in the presence of Lewis acid as catalyst is called Friedel-Crafts acylation. For example, the reaction of benzene with ethanoyl chloride (acetyl chloride) gives the ketone, phenylethanone (acetophenone).

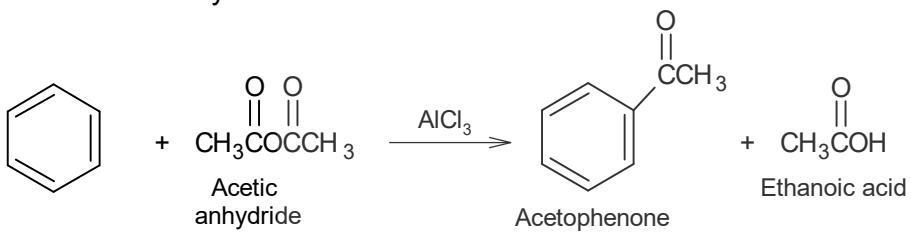


The Friedel-Craft acylation is very important reaction in organic chemistry. It has many applications e.g. It is an excellent method for synthesis of aromatic ketones.

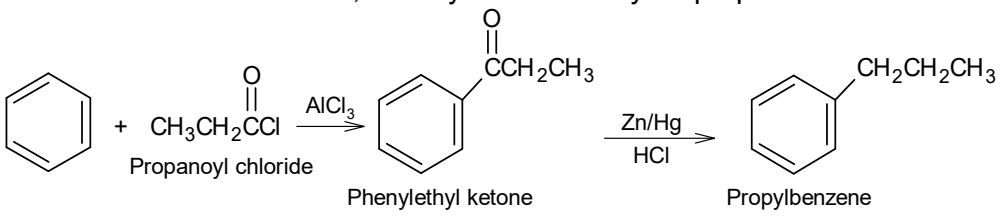
The mechanism of Friedel-Crafts acylation, which we will explain in section 11.3.6, is similar to other electrophilic aromatic substitution reactions. The electrophile in this reaction is the resonance stabilised carbocation, **acylium ion**. This ion is formed when the acid chloride reacts with the Lewis acid, $AlCl_3$.



Carboxylic acid anhydrides can be used as alternative to acid chlorides for the Friedel-Crafts acylation reaction.



Friedel-Crafts acylation reaction is synthetically useful reaction. For example the carbonyl group of the ketone produced by Friedel-Crafts acylation can be reduced to $>CH_2$ group by using zinc amalgam and hydrochloric acid. This method of reduction is known as Clemmensen reduction which you have studied in Unit-10 of this course. By the combination of Friedel-Crafts acylation and Clemmensen reduction, an alkylbenzene may be prepared.



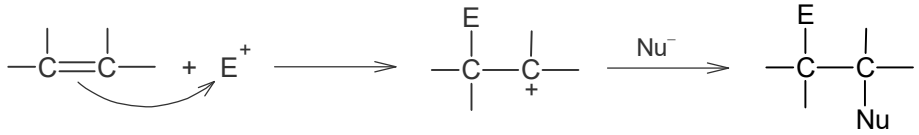
Unlike Friedel-Crafts alkylation, Friedel-Crafts acylation reactions are not accompanied by rearrangements within the acyl group. Moreover, there is no

polysubstitution as the aromatic ring is deactivated after the introduction of the first acyl group. Acylation reactions are free from limitations of alkylation reactions. Secondly, acylium ions do not undergo rearrangements.

11.3.6 Mechanism of Electrophilic Substitution

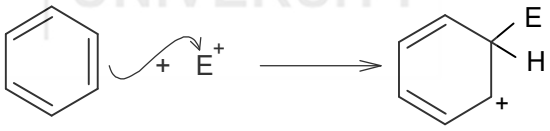
All the electrophilic substitution reactions take place by similar mechanism. It is necessary to understand the principles of this mechanism. Thus, we will discuss the general electrophilic substitution mechanism by using E^+ for electrophilies.

Before studying detailed mechanism, let us briefly recall what we have learnt about electrophilic addition to alkenes. Electrophilic attack on C = C gives carbocation intermediate which is then attacked by nucleophile to yield addition product.

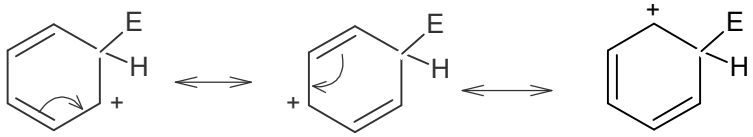


An electrophilic aromatic substitution reaction begins in a similar way. The π electrons of the ring attack on electrophile E^+, forming a σ bond with electrophile. In this process, the positive charge of the electrophile is transferred to the adjacent ring carbon atom which is called carbonation. This is a slow step and is, therefore, the rate determining step.

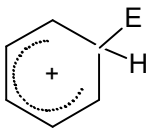
Formation of C—E bond converts sp^2 hybridised carbon to sp^3 hybridised carbon atom of the ring, which disturb the conjugation of benzene ring. Hence, the resulting intermediate is not aromatic.



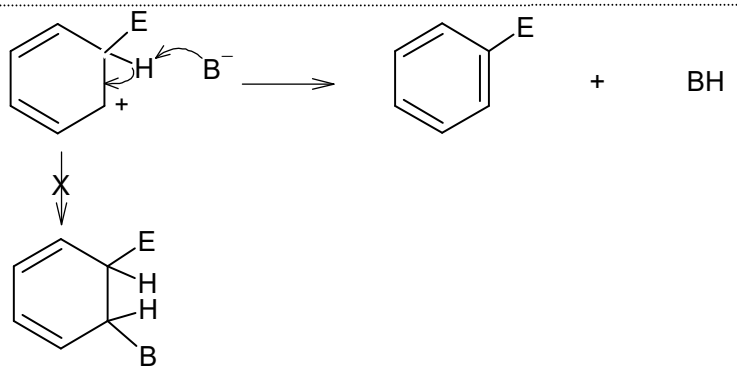
This carbocation is stabilised by resonance as shown below:



These three resonance structures of the intermediate are often combined and represented as follows:



In the case of alkenes, you have seen that nucleophile attacks the carbocation to yield the addition product. Since, in the present case, the addition of the nucleophile would destroy the aromatic stabilisation of the benzene ring, this type of addition does not take place in aromatic carbocations. Instead, nucleophile acts as base and abstracts a ring proton yielding substituted aromatic product.



This reaction is exothermic in nature because C—E bond is stronger than C—H bond. The potential energy diagram (Fig.11.1) of electrophilic substitution reaction of benzene also confirmed that this is an exothermic reaction.

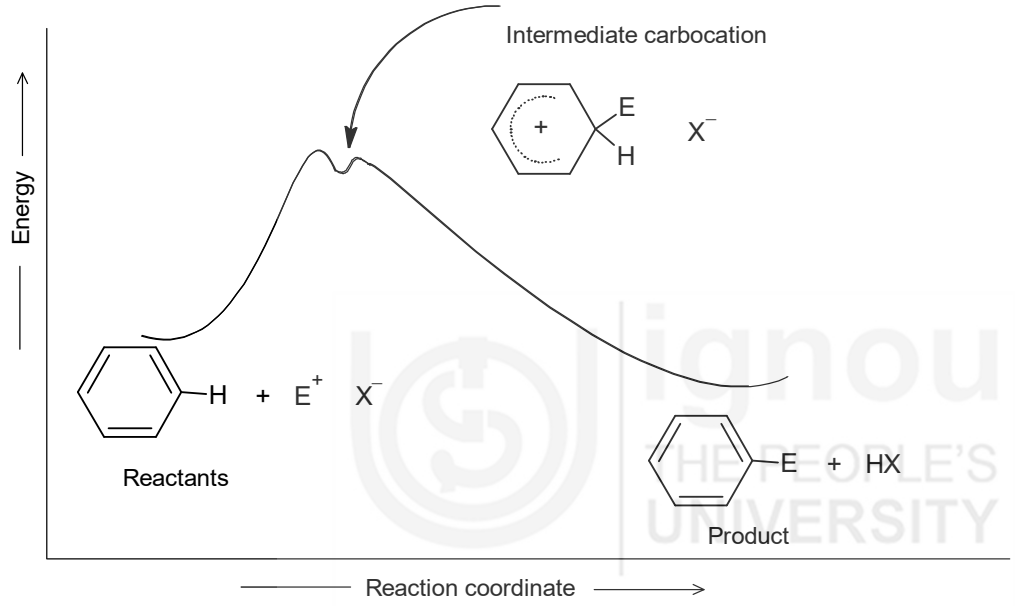
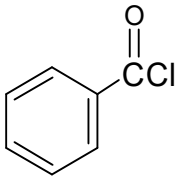


Fig. 11.1: Potential energy diagram for an electrophilic substitution reaction of benzene.

SAQ 5

Give the structure of the product expected from the reaction of each of the following compounds with benzene in the presence of $AlCl_3$.

a) $(CH_3)_2CHCCl$ (O)

b) 

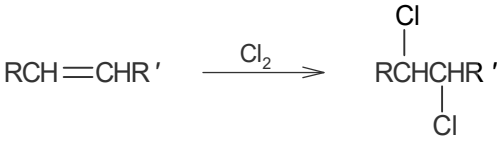
c) $C_2H_5COCC_2H_5$ (O O)

11.4 ADDITION REACTIONS OF BENZENE

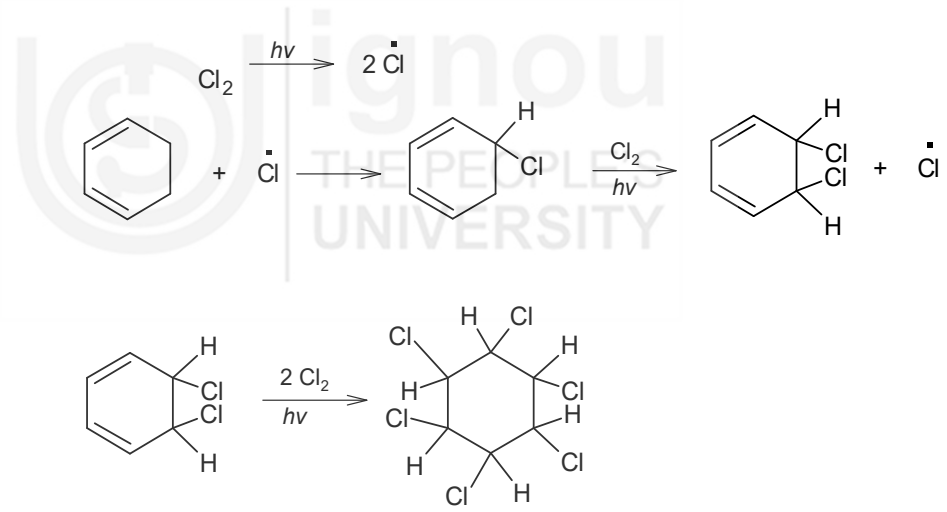
In addition to electrophilic substitution reactions, benzene also undergoes few addition reactions, e.g. addition of halogens to benzene and addition of hydrogen to benzene (reduction of benzene). Let us discuss these reactions in little detail.

11.4.1 Addition of Halogen to Benzene

You have already studied in the first semester that addition of chlorine to an alkene gives 1,2-dichloroalkane.



In contrast to this, the addition of chlorine to benzene takes place with some difficulty and produces several isomers of 1, 2, 3, 4, 5, 6-hexachlorocyclohexanes. In the presence of sunlight, benzene gives an addition product. For example, when treated with chlorine or bromine in the presence of sunlight, benzene forms the benzenehexachloride ($C_6H_6Cl_6$, known as gammaxene) and benzenehexabromide ($C_6H_6Br_6$) respectively. These addition reactions proceed by the free radical mechanism.

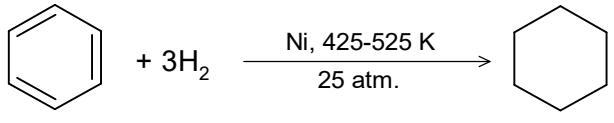


1,2,3,4,5,6-Hexachlorocyclohexane

The 1,2,3,4,5,6-hexachlorocyclohexane, theoretically can exist in eight stereoisomerism forms but only seven of these are known. One of the isomers, is gammaxene, is a powerful insecticide. It is very stable and acts more quickly than DDT. Remember all the isomers exist in chair form.

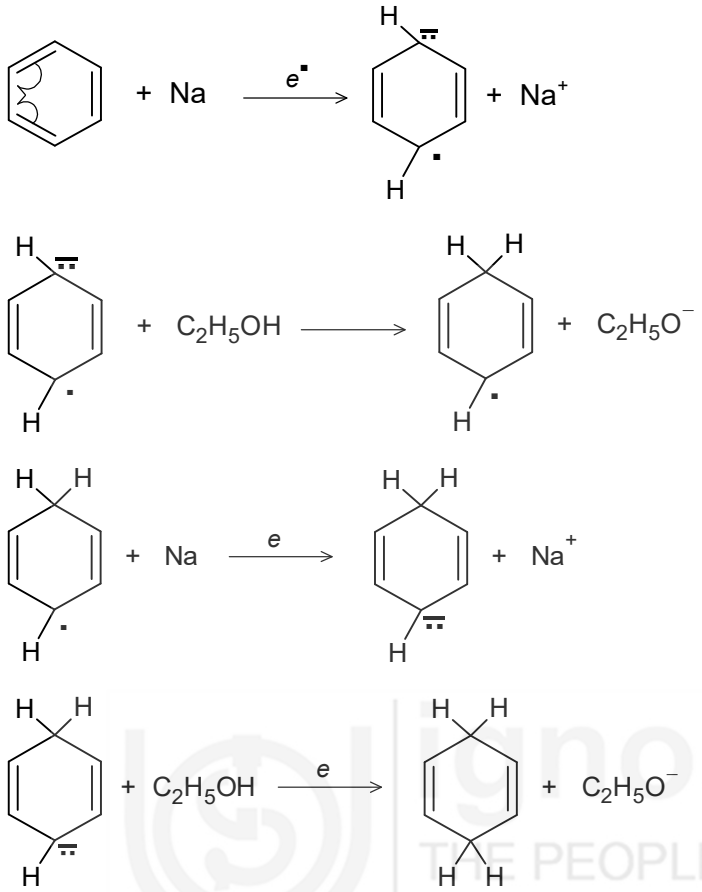
11.4.2 Reduction of benzene

Hydrogenation of benzene at higher temperature and under pressure yields cyclohexane.



Benzene Cyclohexane

Although benzene is not reduced by metals and acid, or by sodium in ethanol, it is reduced by sodium in liquid ammonia in the presence of ethanol (Birch reduction) to give 1, 4-dihydrobenzene (cyclohexa-1, 4-diene). This reaction has also been shown to have free radical mechanism.



Lithium in anhydrous ethylamine, however, reduces benzene to cyclohexene and cyclohexane.

SAQ 6

Give the mechanism of conversion of benzene to cyclohexane.

11.5 SUMMARY

In this unit you have studied that:

- Unlike alkenes, benzene does not undergo addition reactions but it undergoes electrophilic substitution reactions, e.g., nitration, halogenation, sulphonation, Friedel-Crafts alkylation, Friedel-Crafts acylation etc.
- Nitration of benzene gives nitrobenzene. Nitration of benzene can be carried out by reaction of benzene with a mixture of concentrated nitric and sulphuric acids.
- Benzene reacts with halogens in the presence of a catalyst ($AlCl_3$, $FeBr_3$, $FeCl_3$) to give aryl halides. Fluorine is too reactive and a poor yield of

fluorobenzene is obtained. Chlorine reacts smoothly and gives an excellent yield of chlorobenzene. Iodine is unreactive; however, iodination of benzene is carried out in the presence of oxidising agent such as hydrogen peroxide.

- Benzene reacts with SO_3 to give benzenesulphonic acid. Sulphonation is usually accomplished using sulphuric acid or fuming sulphuric acid ($H_2SO_4 + SO_3$) containing varying proportions of sulphur trioxide. Sulphonation is a highly reversible reaction.
- Reaction of aromatic compounds with alkyl halides in presence of anhydrous $AlCl_3$ as catalyst gives alkylated products. This reaction is known as Friedel-Crafts alkylation. This Friedel-Crafts reaction is widely applicable in organic synthesis, but it has some limitations e.g.The first alkyl group activates the ring towards further substitution. Friedel-Crafts alkylation reactions are limited to alkyl halides; aryl halides and alkenyl halides do not react. Sometimes during the alkylation, the attacking electrophile undergoes rearrangement by 1, 2-shift of H or R. Aromatic amines fail to undergo alkylation. If the aromatic compound has an electron withdrawing substituent, it does not undergo Friedel-Crafts alkylation.
- Substitution of an acyl group into an aromatic ring by reaction with acid chlorides in presence of Lewis acid as catalyst is called an aromatic acylation reaction or Friedel-Crafts acylation.
- The addition of chlorine to benzene takes place with some difficulty. In the presence of sunlight, benzene gives an addition product. Several isomers are 1, 2, 3, 4, 5, 6-hexachlorocyclohexanes are obtained.

11.6 TERMINAL QUESTIONS

1. Arrange the following compounds in the expected order of the reactivity towards Friedel-Crafts alkylation.

   CH_3CH_2Br, CH_3CH_2Cl, CH_3CH_2I, CH_3CH_2F

2. How do you convert benzene to the following compounds?

   a) Bromobenzene
   b) Benzenesulphonic acid
   c) Cyclohexane
   d) Ethylbenzene
   e) Hexachlorocyclohexane

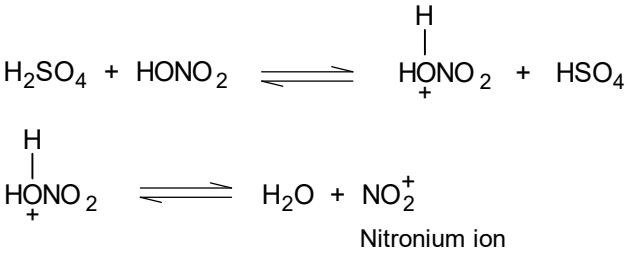
3. Write the mechanism of sulphonation of benzene using SO_3 as electrophile.

11.7 ANSWERS

Self-Assessment Questions

1. The electrophile in this reaction is the nitronium ion, NO^+_2. It is

generated by the reaction of H_2SO_4 with HNO_3.



Nitronium ion

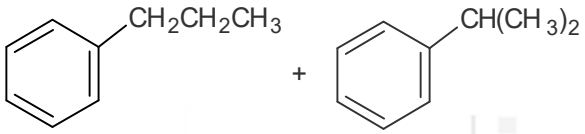
2. i) aryl halide

   ii) halogen-halogen

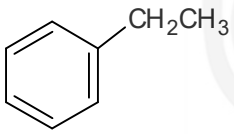
3. i) E3lectrophilic

   ii) hot aqueous

4. a) No reaction.

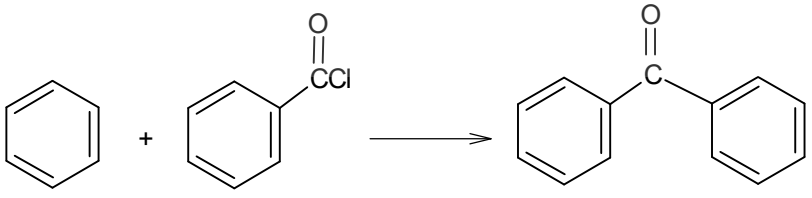
   b) 

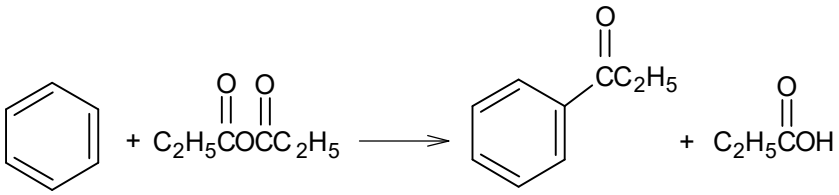
   Minor Major

   c) 

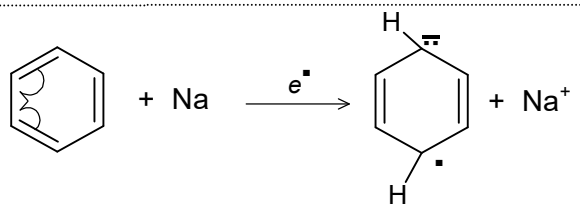
   d) No reaction.

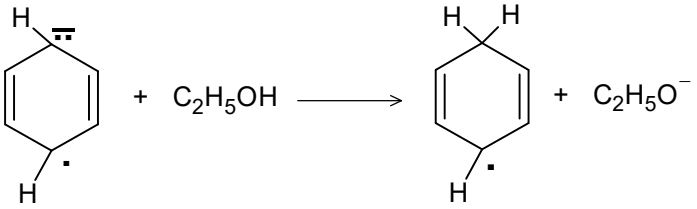
5. a) 

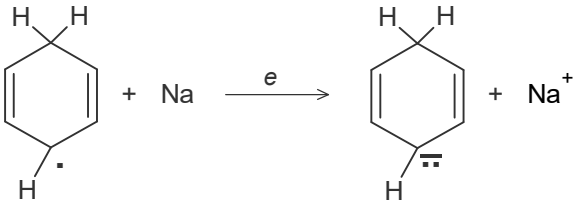
   b) 

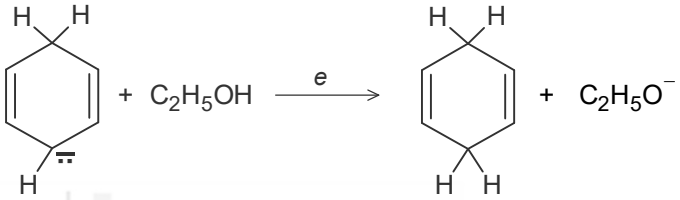
   c) 

6).









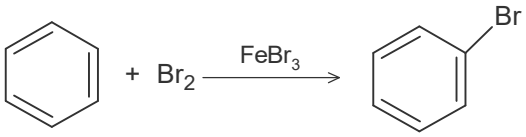
Similarly, following same step we get cyclohexane.

Terminal Questions

1. Reactivity increases as follows:

   $CH_3CH_2I < CH_3CH_2Br < CH_3CH_2Cl < CH_3CH_2F$

2. a)



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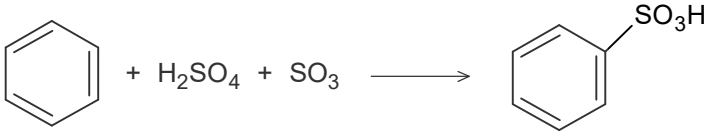

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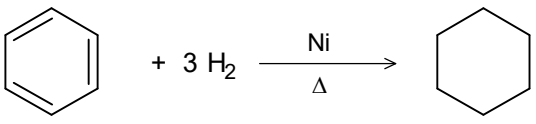

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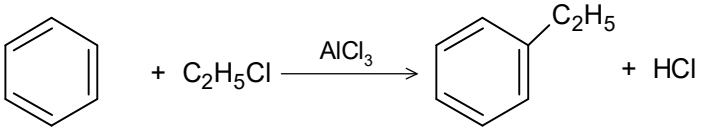

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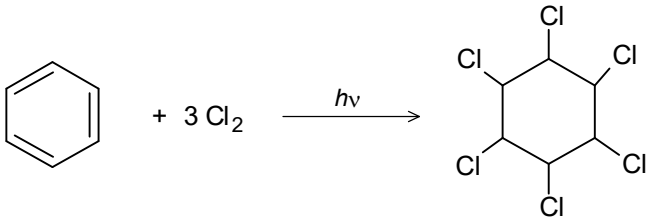
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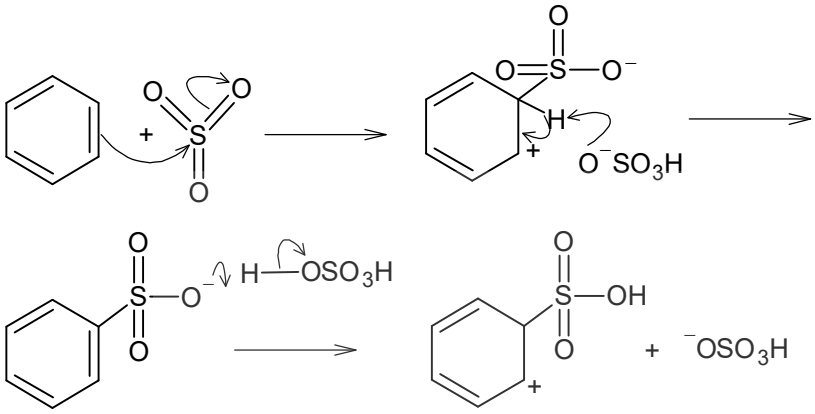
O
S
O
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O
O
S
O⁻
H
O⁻SO3H
O
S
O⁻
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OSO3H
O
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OH
O
+
⁻OSO3H

UNIT 12

REACTIONS OF AROMATIC COMPOUNDS - II

Structure

12.1 INTRODUCTION

In the last unit, Unit 11, we have learnt some important reactions of aromatic compounds. There are two main types of substitution reactions in aromatic compounds i.e. i) substitution reactions at aromatic ring and ii) substitution reactions at the side chain of aromatic ring. In that unit, we have also discussed electrophilic substitution reactions on benzene ring. In this unit, we will explain the effect of substituents on reactivity and orientation of aromatic compounds. In the next section we will consider the meaning of *ortho, para* and *meta* directing activators/deactivators. In addition to this, we will study the substitution reactions of side chain of aromatic compounds. You will notice that the substitution of side chain follows free radical mechanism while substitution at ring carbon follows ionic mechanism. In the last section, we will discuss the oxidation of side chain of aromatic compounds.

Expected Learning Outcomes

After studying this unit, you should be able to:

- explain the effect of substituents on reactivity;
- explain the effect of substituents on orientation;

- ❖ state the concept of *ortho, para and meta* directing activator/deactivator;
- ❖ describe the substitution in the side chain of aromatic compounds; and
- ❖ explain the oxidation reactions of the side chain.

12.2 EFFECT OF SUBSTITUENTS ON REACTIVITY AND ORIENTATION

Benzene forms only one monosubstituted product by the electrophilic substitution. Let us see what happens when we carry out an electrophilic substitution on a substituted benzene. Studies have shown that the substituents effect the reactivity and the orientation in the benzene ring. Three possible disubstituted products, viz., *ortho*, *para* and *meta* can result. These three products are not formed at random; rather, a given substituent already attached to the benzene ring usually directs the position of the second substituent. There are two types of substituents – one is electron-donating groups, such as $-NR_2$, $-OH$, $-OR$, $-NHCOR$, and alkyl groups and other is electron-withdrawing groups which include halogens, $-CHO$, $-COR$, $-COOR$, $-CN$, $-NO_2$, $-\overset{+}{N}R_3$ etc..

Now we will study the effect of substituents on reactivity and orientation.

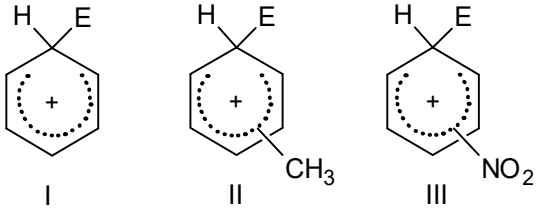
12.2.1 Effect of Substituents on Reactivity

To compare the rates of electrophilic substitution in benzene, methyl substituted benzene (methylbenzene or toluene) and nitro substituted benzene (nitrobenzene) are compared in a reaction, say nitration. It is found that nitration of methylbenzene (toluene) is more facile than benzene whereas nitration of nitrobenzene is more difficult than benzene. In other words, benzene ring seems to be activated in methylbenzene and deactivated in nitrobenzene. If we compare the reactivities of benzene, methylbenzene and nitrobenzene towards nitration reaction, we find the following order:

methylbenzene > benzene > nitrobenzene

i.e., as compared to benzene, methylbenzene is more reactive while nitrobenzene is less reactive. CH_3 group is called an activating group, while NO_2 is a deactivating group for electrophilic substitution of aromatic compounds. By and large, the *meta* directing groups are deactivating and the *ortho* and *para* directing groups are activating, with the exception of halogens.

Let us see if we can explain this on the basis of the intermediate carbocation formed.

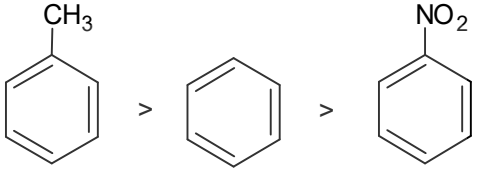


I II III

In the case of methylbenzene (II), the methyl group, which is an electron-donating group, tends to neutralise the charge on the carbocation, this

dispersal of the charge stabilises the carbocation thus leading to faster reaction than benzene.

In case of nitrobenzene (III), the NO_2 group which is electron-withdrawing group, tends to intensify the positive charge and destabilise the carbocation. Due to this effect, the rate of the reaction is slower than in benzene. Reactivity in electrophilic aromatic substitution depends therefore then, upon the tendency of a substituent group to release or withdraw electrons. A group that releases electrons activates the ring while a group that withdraws electrons deactivates the ring. Hence, the order of reactivity of the above compounds towards electrophilic substitution reaction is:

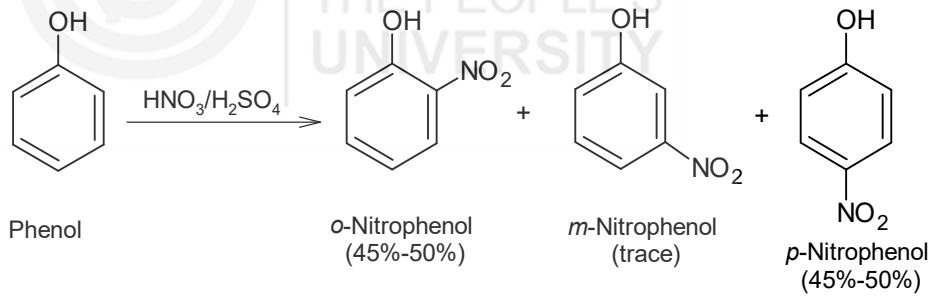


SAQ 1

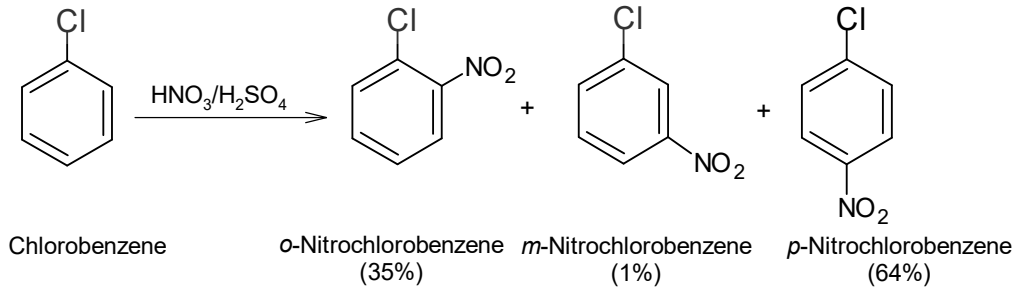
Which compound would you expect to undergo aromatic nitration more readily, C_6H_6 or $C_6H_5CCl_3$ and why?

12.2.3 Effect of Substituents on Orientation

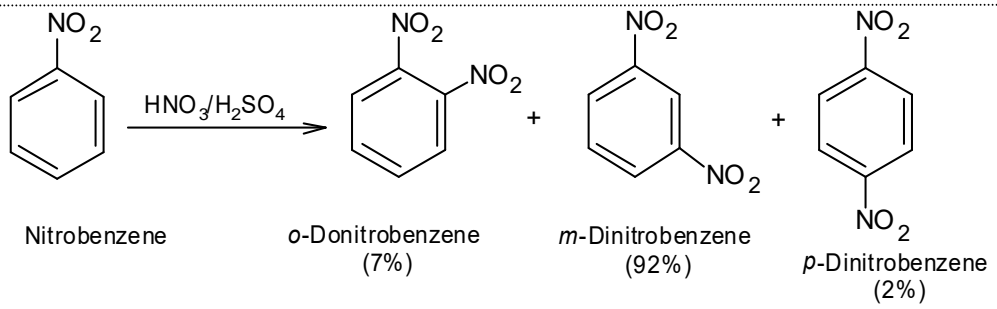
The second effect of a substituent is to direct the position of the incoming substituent. Thus, for instance, nitration of phenol gives *ortho*- and *para*-nitrophenols as major products.



Halogens are unusual in their effect on electrophilic aromatic substitution, we will discuss it under the heading "*ortho* and *para* directing deactivators" of this section . Nitration of chlorobenzenes yields *ortho*-chlorobenzene and *para*-chlorobenzene as the major products.



On the other hand, nitration of nitrobenzene yields *meta*- dinitrobenzene as the major product, i.e.,



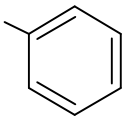
Nitrobenzene | *o*-Donitrobenzene (7%) | *m*-Dinitrobenzene (92%) | *p*-Dinitrobenzene (2%)

This shows that different substituents have different effect on the substitution reaction. Thus substituents can be classified into three the following groups. i.e.

- *ortho* and *para*-directing activators
- *ortho* and *para*-directing deactivators
- *meta*-directing deactivators

Table 12.1 gives a list of substituents with their directive influence and also whether they activate or deactivate the ring.

Table 12.1: Lists some of the groups in each category

***Ortho-* and *para*-directing activators**	***Ortho-* and *para*-directing deactivators**	***Meta*-directing deactivators**
$-NH_2$	$-I$	$-N^+(CH_3)_3$
$-OH$	$-Br$	$-NO_2$
$-OCH_3$	$-Cl$	$-CN$
$-NHCOCH_3$	$-F$	$-COCH_3$
		$-COOCH_3$
		$-COOH$
		$-CHO$
$-CH_3$		

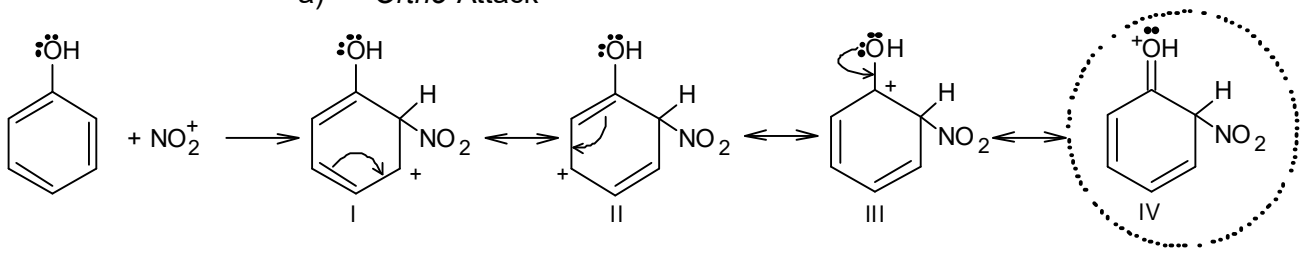
Before we try to account for the orientation in electrophilic substitution, we should clarify our concept of activating and deactivating groups. Remember activating groups activate all the positions of the ring. They are *ortho* and *para* directors because they activate *ortho* and *para* position much more than they do the *meta* position. Similarly, deactivating groups deactivate all positions in the ring. They are *meta* directors because they deactivate the *ortho* and *para* position more than they deactivate *meta* position. Thus, the effect of any group, whether activating or deactivating, is strongest at the *ortho* and *para* positions.

Ortho- and *para*-directing activators:

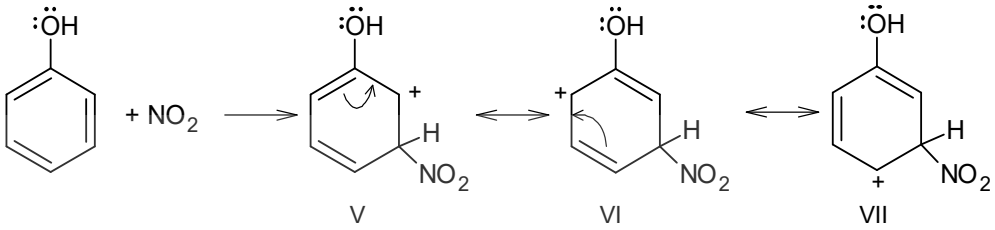
To understand the orientation effect of the substituents, we have to first write all the possible resonance forms of the charged intermediates (carbocations) for each of the three possible reaction courses.

Let us take the example of nitration of phenol. Reaction of NO_2^+ at the *ortho, meta* and *para* positions of phenol gives the intermediate, carbocation with the following resonance structures:

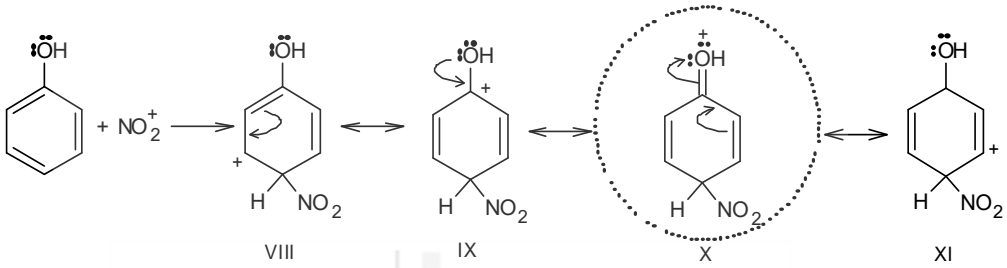
a) *Ortho*-Attack



b) *Meta*-Attack



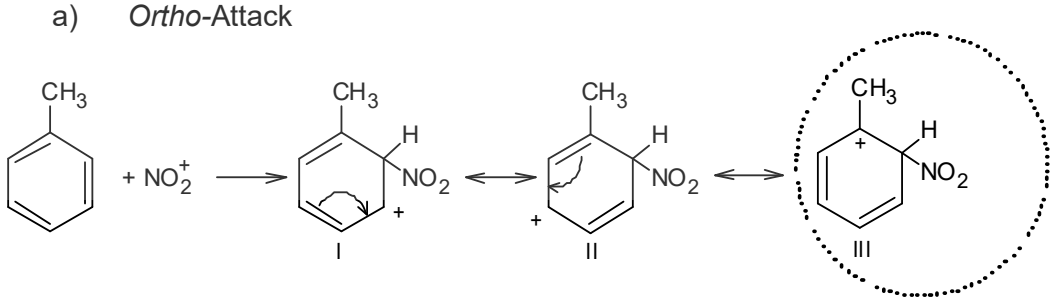
c) *Para*-Attack



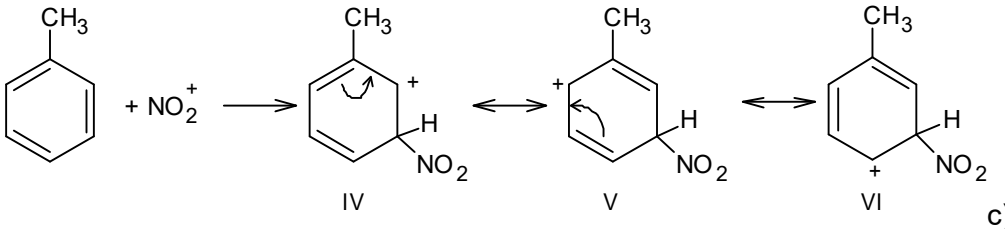
In case of *ortho* and *para* attacks, structures IV and X respectively show that the unshared electron pair of oxygen delocalizes the positive charge of the carbocation and, hence, four resonance structures are possible. In the case of *meta* attack, lone pairs of oxygen are not involved in the delocalisation of positive charge. Hence, the carbocation that is formed has only three resonance structures, therefore, *ortho*- and *para*- nitrophenols are the major products.

Now take the example of electrophilic aromatic substitution on alkyl substituted benzene ring. Let us inspect the possible resonance structures of carbocation formed by the attack of the electrophile, NO_2^+, on toluene.

a) *Ortho*-Attack

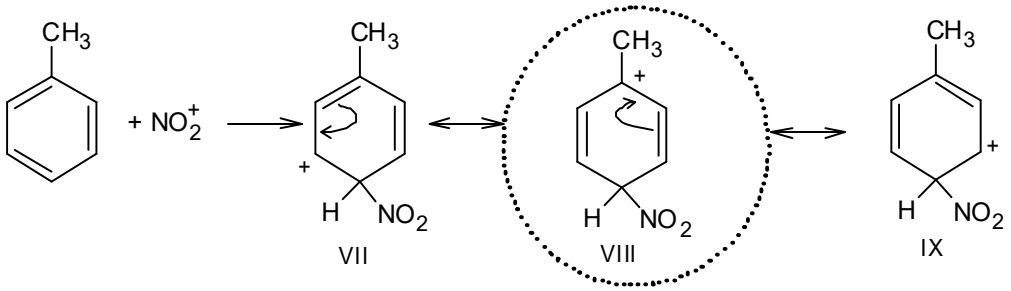


b) *Meta*-Attack



c)

Para-Attack



As indicated above, in structures III and VIII, resulting from *ortho* and *para* attacks respectively, the positive charge is located on the carbon atom to which the methyl group is attached. Because that structure has tertiary carbocation character, it is more stable than the others' in which the positive charge is at a secondary carbocation. On the other hand, *meta* attack produces an intermediate in which none of the resonance structures benefits from such tertiary carbocation stabilisation. Thus, electrophilic attack on a carbon located *ortho* or *para* to methyl group leads to a cationic intermediate that is more stable than the one derived by attack at the *meta* carbon. Substitution at *ortho*- and *para*-position is, therefore, preferred to the *meta*-substitution.

This can also be explained on the basis of inductive effect. The carbocations III and VIII formed by the *ortho*- and *para*-attacks respectively are stabilised by inductive effect of methyl group and are therefore, formed in major amount.

Let us understand this on the basis of potential energy diagram for nitration of methylbenzene (Fig. 12.1). The carbocations formed from attack at *ortho* and *para* positions of toluene are more stable than the carbocation formed from *meta* position. However, all the three carbocations obtained from methylbenzene are more stable than the carbocation obtained from benzene.

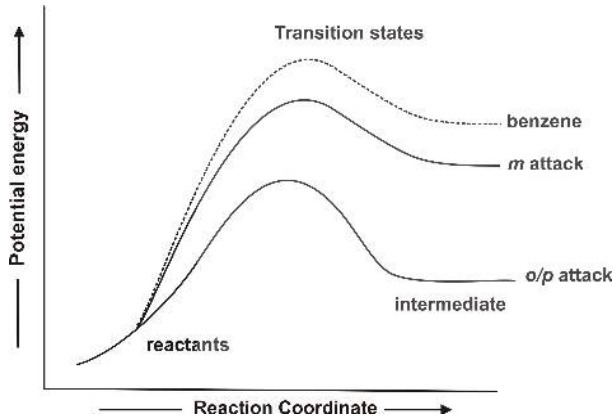
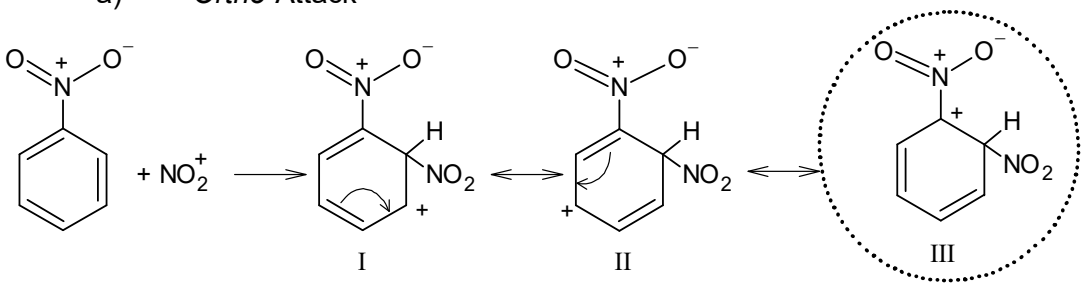


Fig. 12.1: Schematic potential energy diagram for AESR in benzene (----------) and methylbenzene (———)

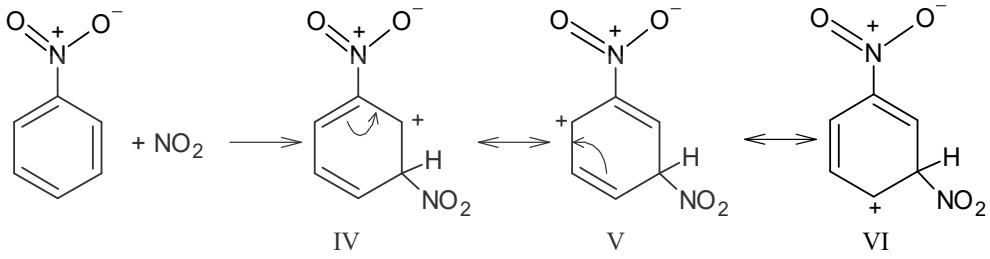
Meta-directing deactivators:

We can apply similar arguments to *meta*-directing groups. These groups are all electronegative groups without an unshared electron pair on an atom adjacent to the benzene ring. In all these cases, the benzene ring would be deactivated. Let us take the example of nitration of nitrobenzene. The possible resonance structures of the carbocation formed are as follows:

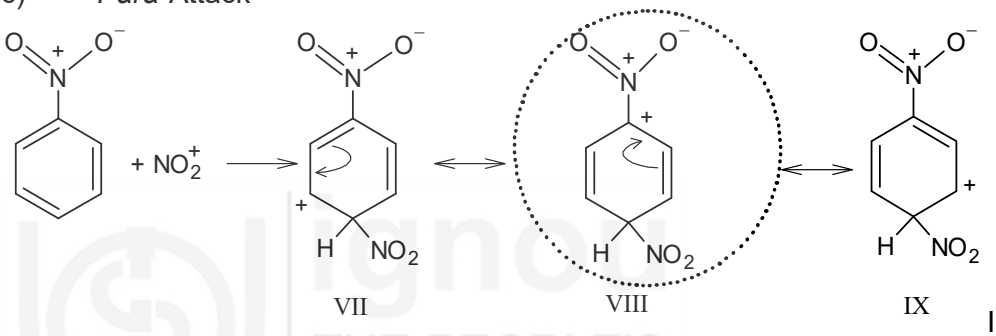
a) *Ortho*-Attack



b) *Meta*-Attack



c) *Para*-Attack



In all the three cases, carbocations formed have three resonance structures. But the structures III and VIII resulting from *ortho* and *para* attack, respectively, are very unfavourable because the positive charge is placed directly on the carbon carrying the electron withdrawing group. A severe electrostatic repulsive interaction between the carbocation and the positive end of the NO_2^+ group strongly disfavours these carbocations. However, the carbocations formed by *meta* attack, have no such form with similar charges on adjacent atoms. Therefore, its transition state is the most stable, and attack at *meta*-position is preferred. Potential energy diagram of the reaction is shown in Fig. 12.2. The carbocation obtained from *meta* attack is more stable than the *ortho* and *para* attack.

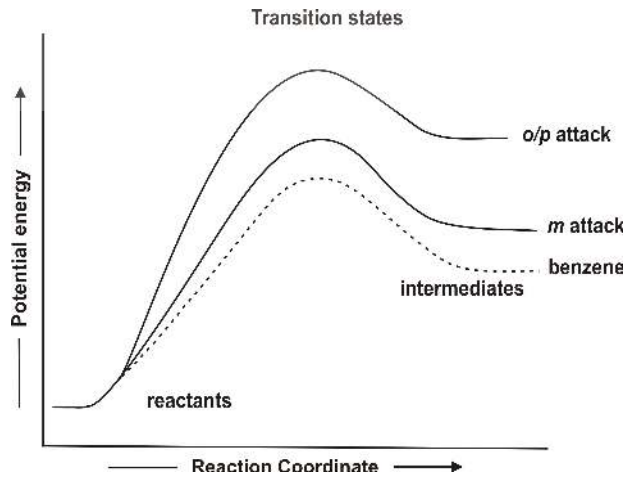
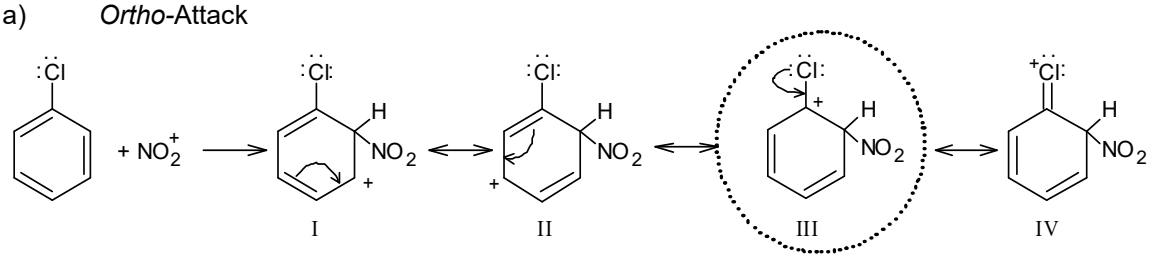


Fig. 12.2: Schematic potential energy diagram for AESR in benzene (-----) and nitrobenzene (——)

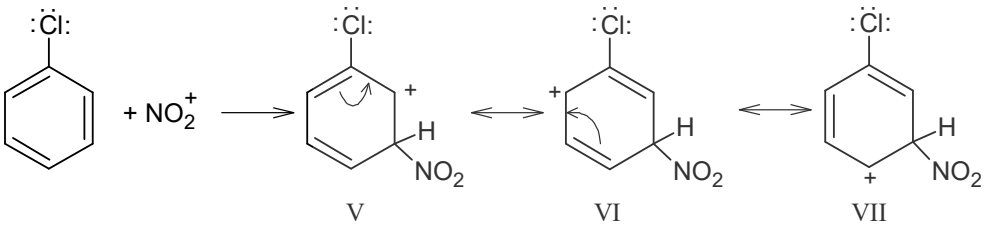
***Ortho* and *para* directing deactivators:**

Halogens are unusual in their effect on electrophilic aromatic substitution. They are deactivating yet *ortho* and *para* directing. For understanding the orientation, consider the attack of electrophile at *ortho*, *meta* and *para* position of chlorobenzene.

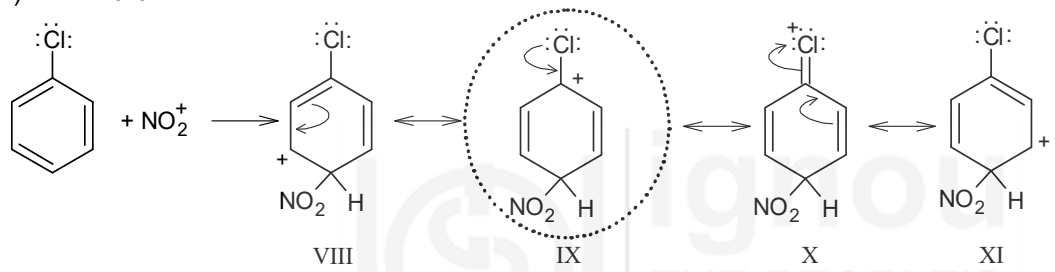
a) *Ortho*-Attack



b) *Meta*-Attack



c) *Para*-Attack



In structures, III and IX, resulting from *ortho* and *para* attacks respectively, there is a positive charge on carbon bearing the halogen atom. Through its inductive effect, chlorine withdraws electrons, making this structure unstable. But there is another factor that one should not forget. It is known that halogens can share a lone pair of electrons and accommodate the positive charge, as shown in structures IV and X, for *ortho* and *para* attacks, respectively. These structures are comparatively stable. No such structure is possible when the electrophiles attack on *meta* position. Structures IV (in *ortho* attack) and X (in *para* attack) outweigh the instability rendered by structures III and IX. Therefore, attack at *ortho* and *para* position is preferred. The potential energy diagram of this reaction is shown in Fig. 12.3. The carbocation obtained from *ortho* and *para* attack is more stable than the carbocation obtained from attack at *meta* position.

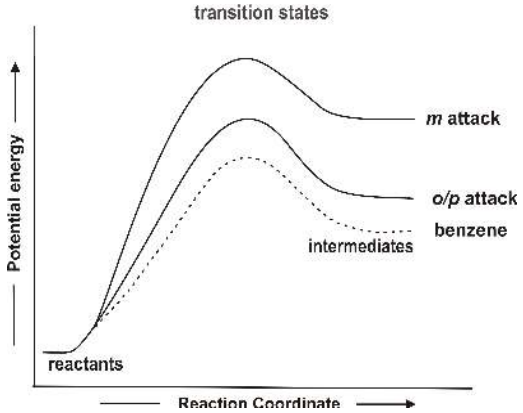


Fig. 12.3: Schematic potential energy diagram for AESR in benzene (----------) and chlorobenzene (———)

SAQ 2

Predict the major and minor products of the following reactions:

a) Nitration of bromobenzene

b) Nitration of nitrobenzene

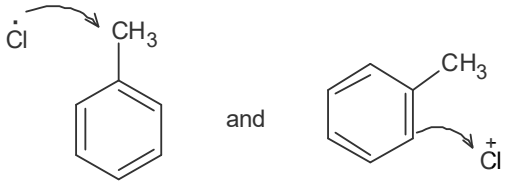
c) Bromination of nitrobenzene

d) Chlorination of pheno

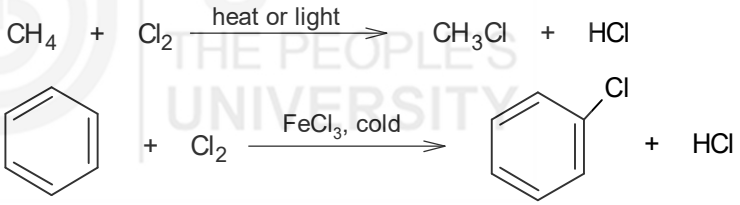
12.3 REACTIONS OF SIDE-CHAIN

12.3.1 Substitution in the Side Chain

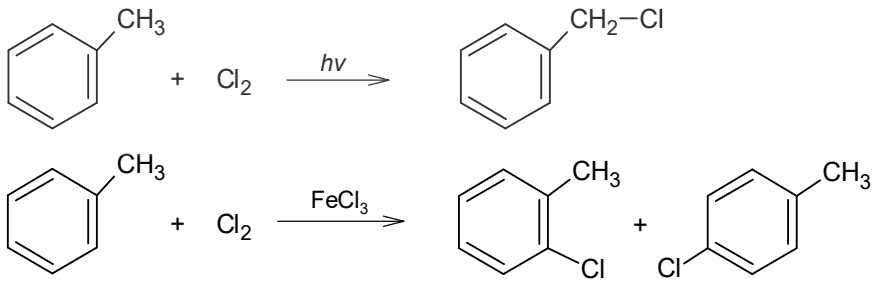
Alkylbenzene clearly offers two position for attack by halogen: the ring and the side chain.



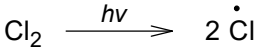
We can control the position of attack by choosing the proper reaction conditions. Halogenation of an alkane requires condition under which halogen atoms are formed by homolyses of halogen molecules, that is, high temperature or light. Halogenations of benzene, on the other hand, involve transfer of positive halogen, which is promoted by Lewis acid catalyst like ferric chloride.

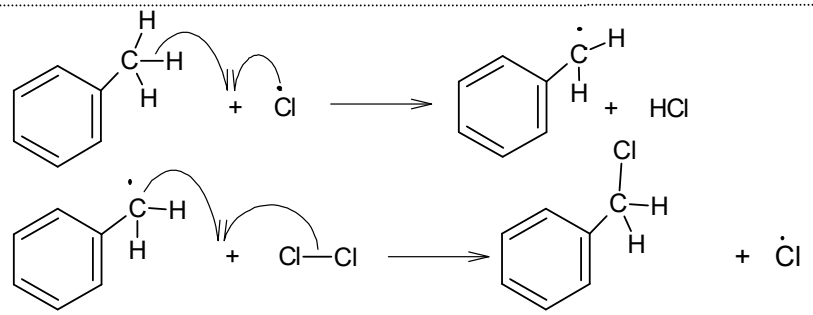


The position of attack in methylbenzene (toluene) would be decided by the nature of the attacking particle and by the condition employed. If the reaction is carried out in the presence of light, substitution occurs almost exclusively in the side chain. In the absence of light and in the presence of ferric chloride, substitution occurs mostly in the ring, for example:

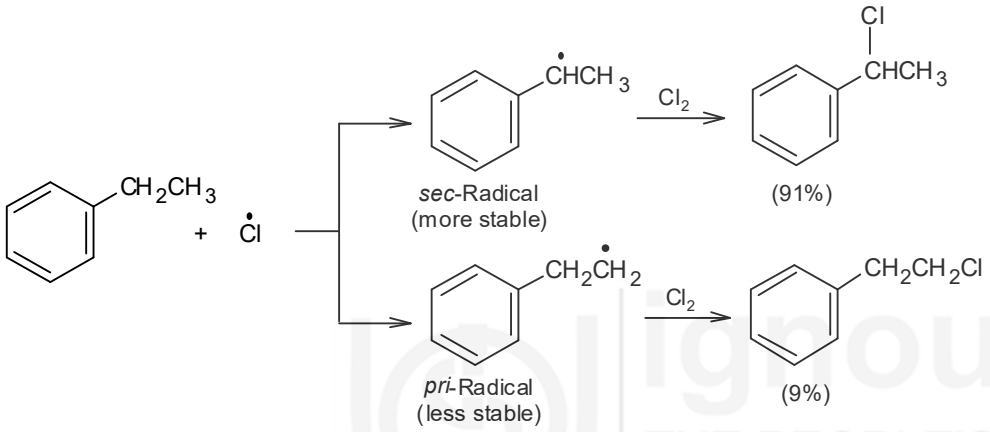


Chlorination of methylbenzene (toluene), in the presence of light, takes place *via* free radical chain mechanism as shown below:

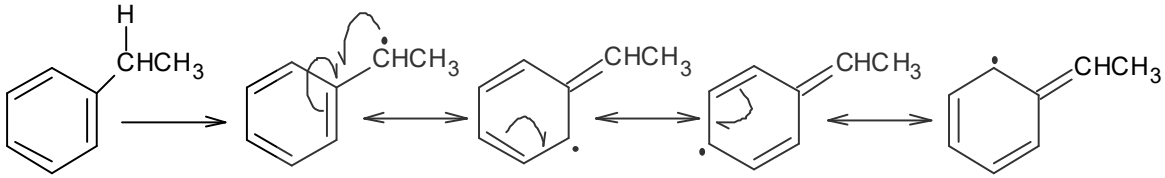




In alkylbenzenes, with side chains larger than methyl, it is expected that the free radical substitution may take place on any of the side chain carbon atoms; so we must consider the likelihood of obtaining a mixture of isomers. For example, chlorination of ethylbenzene should give two isomeric products, 1-chloro-1-phenylethane and 2-chloro-1-phenylethane in equal amounts. But 1-chloro-1-phenylethane is the major (91%) product becouse of the stabilisation of free radical intermediate.



You can ask, why is it so? This is because the bond dissociation energy of benzylic C—H bond, $C_6H_5CH(CH_3)H$, (355 kJ mol^{-1}) is less than β-phenyl ethyl C—H bond, $C_6H_5—CH_2CH_2—H$ (435 kJ mol^{-1}). That means, less energy is required for the homolylic fission of benzylic C—H bond. In other words, benzyl radical is more stable. The greater stability of benzyl radical is due to delocalisation of the odd electron over the ring as shown below:



Since the benzylic radical formed is more stable, 1-chloro-1-phenylethane is the major product.

SAQ 3

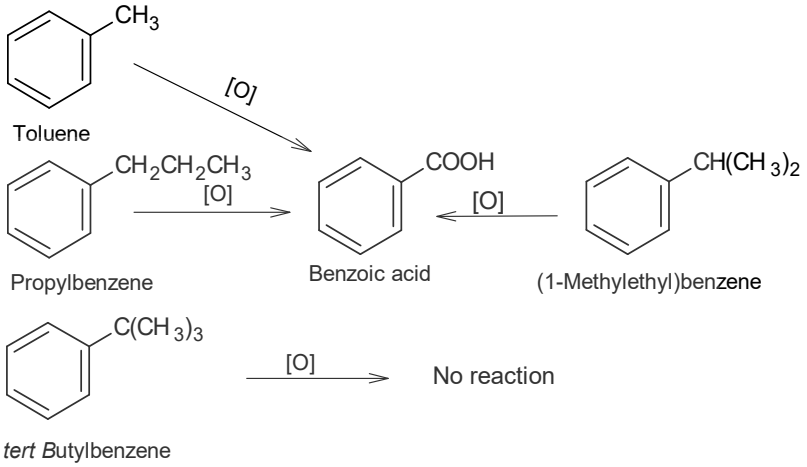
Write the mechanism of chlorination of methyl benzene.

12.3.2 Oxidation of Side-chain

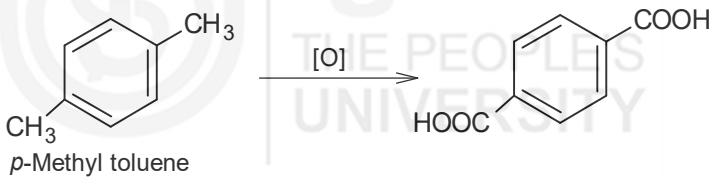
Although benzene is quite unreactive towards the usual oxidising agents ($KMnO_4$, $K_2Cr_2O_7$ etc.), the benzene ring renders an aliphatic side chain quite susceptible to oxidation. The side chain, irrespective of its length is oxidised to

a carboxyl group (−COOH). Tertiary alkyl substituted aromatic compounds do not undergo this reaction. For example, toluene, propylbenzene, (1-methylethyl)benzene are oxidised to benzoic acid in high yields. *p*-Methyltoluene on oxidation gives terephthalic (benzene-1,4-dicarboxylic) acid but tertiary butylbenzene is not effected.

The number and the position of the carboxylic groups produced indicate the number and position of alkyl chain(s) attached to the aromatic ring.

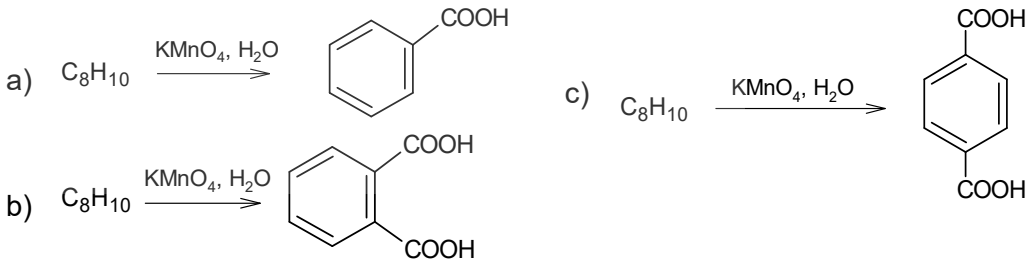


Terephthalic acid is used for the production of polyester fibres in industries. Remember for industrial purposes Terephthalic acid is prepared from *p*-xylene by simple oxidation using air as the oxidant and Co(III) salt as a catalyst .



SAQ 4

Draw the structural formulas for the starting materials in the following reaction:



12.4 SUMMARY

- Alkylbenzenes offer two main areas for attack by halogen–the ring and the side chain.
- In the presence of light, halogen goes to side chain while in the presence of acid catalyst it goes to ring.

- Substituents affect the reactivity and the orientation in the benzene ring.
- A given substituent already attached to the benzene ring usually directs the position of the second substituent.
- There are two types of substituents – one is electron donating group, such as as $-NR_2$, $-OH$, $-OR$, $-NHCOR$, and $-R$ and other is electron withdrawing groups which include halogens, $-CHO$, $-COR$, $-COOR$, $-CN$, $-NO_2$, $-\overset{+}{N}R_3$ etc.
- Besides being different in their 'directing' tendencies,$-CH_3$ and $-NO_2$ groups differ in one more aspect and that is the rate of the reaction. Rate of nitration of benzene, methylbenzene and nitrobenzene is as follows:
- Methylbenzene > benzene > nitrobenzene
- The second effect of a substituent is to direct the position of the incoming substituent. Thus, nitration of phenol gives *ortho* and *para*-nitrophenol as major products. On the other hand, nitration of nitrobenzene yields *meta* dinitrobenzene as the major product,
- This shows that different substituents have different effect on substitution reaction. Thus substituents can be classified into three groups. i.e.,
- *ortho* and *para*-directing activator
- *meta*-directing deactivator
- *ortho* and *para*-directing deactivator
- The side chain, irrespective of its length, is oxidised to a carboxyl group (-COOH).
- Tertiary alkyl substituted aromatic compounds do not follow oxidation reaction.

12.5 TERMINAL QUESTIONS

1) Write equation to show how the following conversion takes place.

   a) Methylbenzene to *m*-bromobenzonic acid

   b) benzene to *p*-nitrotoluene

   c) benzene to *m*-nitrocetophenone

2) Write the chemical equation for the oxidation of the following compounds with hot $KMnO_4$.

   a) *n*-Butylbenzenes

   b) 1,1-Dimethylethyl benzene

   c) 1,3,5-Trymethylbenzene

3) Write the resonance structures of cation formed from $C_6H_5NH_2$ during:

   a) *ortho*-bromination

b) *meta*-bromination

c) *para*-bromination

4) Compound A, B and C are the three isomeric dibromobenzenes. Identify which is *ortho*, *para* and *meta* from the number of mononitration products.

a) Compound A $\xrightarrow{HNO_3/H_2SO_4}$ two mononitration products

b) Compound B $\xrightarrow{HNO_3/H_2SO_4}$ three mononitration products

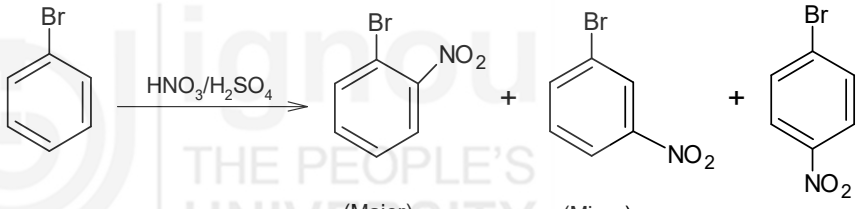
c) Compound C $\xrightarrow{HNO_3/H_2SO_4}$ one mononitration products

12.6 ANSWERS

Self-Assessment Questions

1. While the $-CH_3$ group is electron releasing and activates the ring, the CCl_3 group is strongly electron withdrawing because of the influence of the electronegative chlorine atoms and hence, deactivates the ring. Therefore, $C_6H_5CCl_3$ undergoes substitution more slowly.

2. a)



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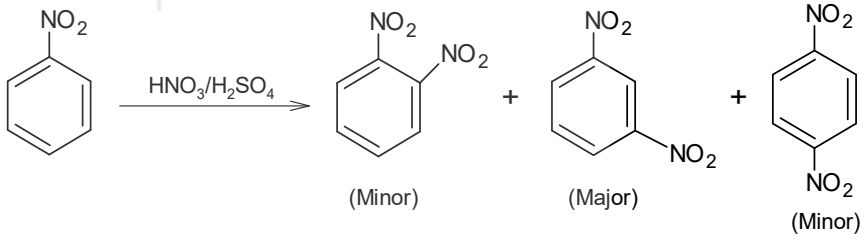

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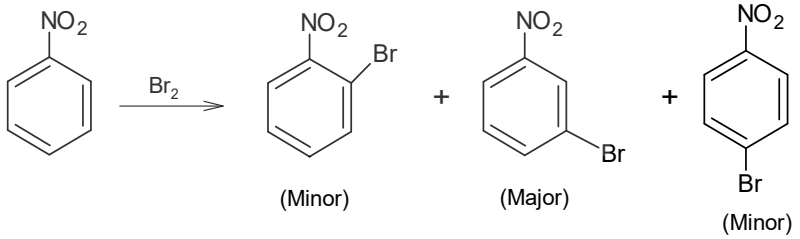

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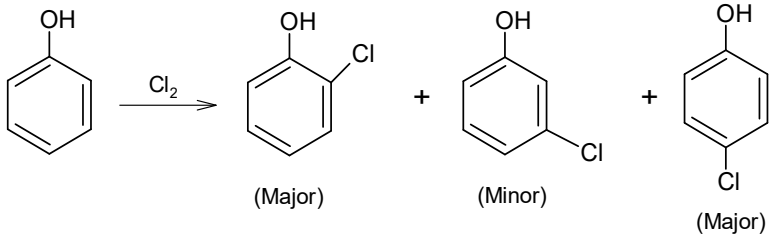
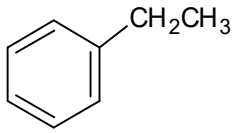
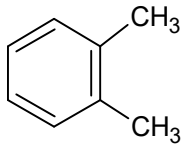
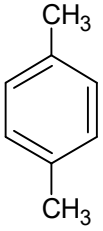


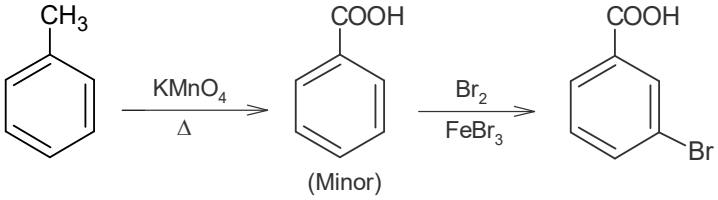
3. See Sub-Sec. 12.3.1

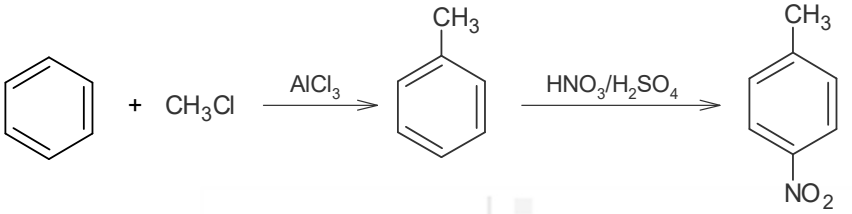
4. a) 

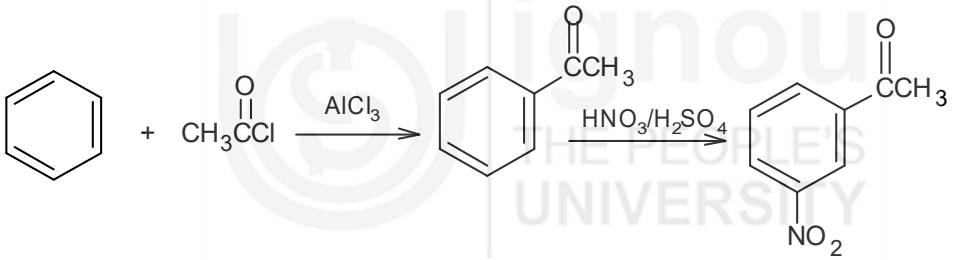
b) 

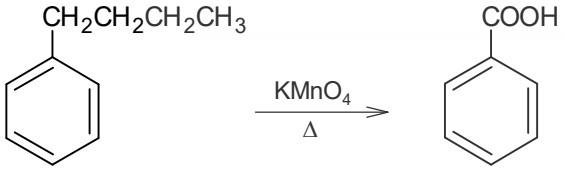
c) 

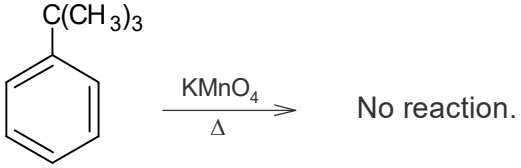
Terminal Questions

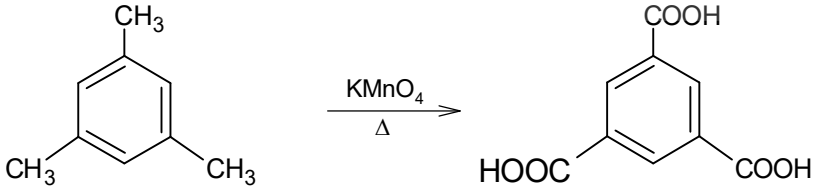
1. a) 

b) 

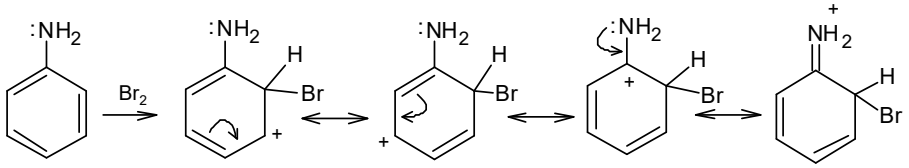
c) 

2. a) 

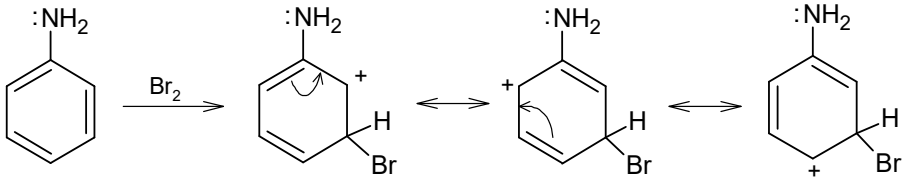
b) 

c) 

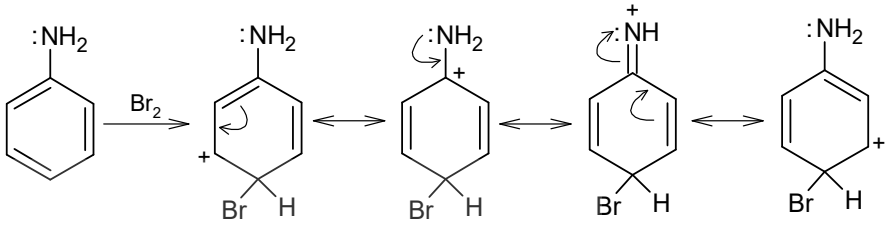
3. a) *Ortho*-Attack



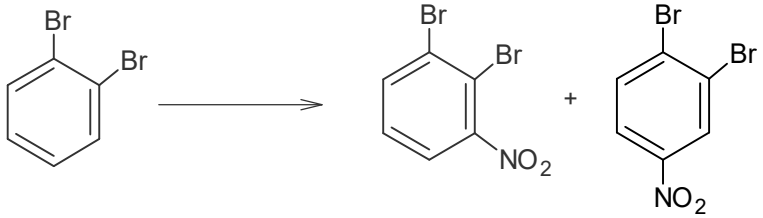
b) *Meta*-Attack



c) *Para*-Attack

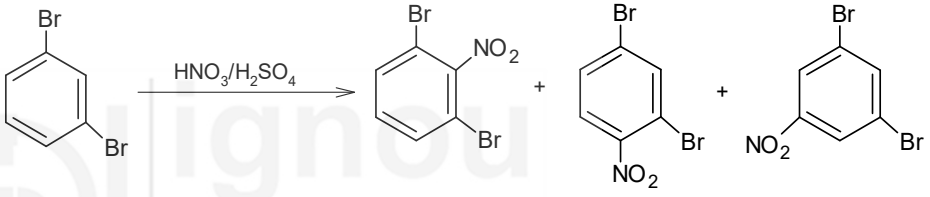


4) a)



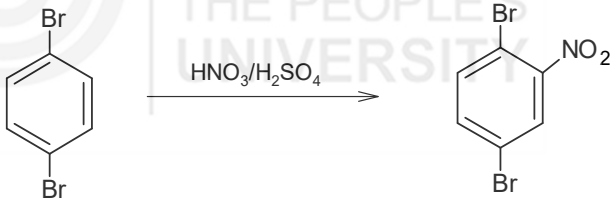
Only these two products are possible from *o*-dibromobenzene

b)



Three products are possible from *m*-dibromobenzene

c)



Only one product is possible from *p*-dibromobenzene

On the basis of above reactions, we can say that:
Compound A is a *o*-dibromobenzene
Compound B is a *m*-dibromobenzene
Compound C is a *p*-dibromobenzene.

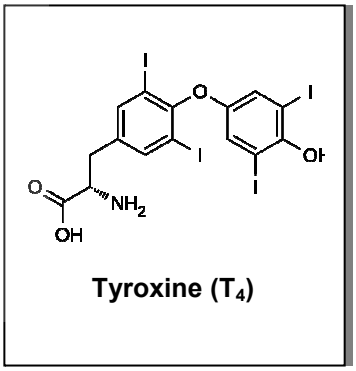
UNIT 13

ALKYL HALIDES

Structure

13.1 INTRODUCTION

In earlier units of this Block, we have described the preparations and reactions of aromatic hydrocarbons. In this unit and in the next units, we will study halogen derivatives of hydrocarbons. Replacement of one or more hydrogen atoms in a hydrocarbon by halogen atom(s) [F, Cl, Br, or I] gives the halogen derivatives. These compounds are important laboratory and industrial solvents and serve as intermediates in the synthesis of other organic compounds. Many chlorohydrocarbons have acquired importance as insecticides. Although there are not many naturally occurring halogen derivatives, yet you might be familiar with one such compound, thyroxine (T_4)-a thyroid hormone.



Tyroxine (T_4)

In this unit, we shall take up the chemistry of the alkyl halides in detail. We shall begin with classification of halogen derivatives and go over to methods of the preparation of alkyl halides. We shall also discuss the reactivity of these halogen compounds and our main focus will be, on some important reactions such as nucleophilic substitution (S_N) and elimination (E) reactions. Finally, we shall take up uses of halogen derivatives and the methods for their detection.

Expected Learning Outcomes

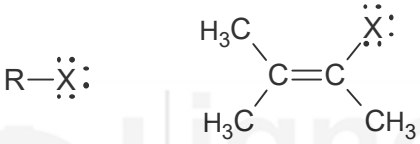
After studying this unit, you should be able to:

- classify the halogen derivatives;

- ❖ outline the methods of preparation of alkyl halides;
- ❖ list the physical properties of halogen derivatives;
- ❖ describe the reactions of alkyl halides, specially nucleophilic substitution and elimination reactions in detail;
- ❖ list and describe the industrial uses of halogen derivatives; and
- ❖ describe the laboratory detection of halogen derivatives.

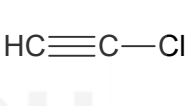
13.2 CLASSIFICATION OF HALOGEN DERIVATIVES

The halogen derivatives are conveniently divided into three classes depending upon the nature of the hydrocarbon residue to which the halogen atom is attached: (i) Alkyl halides (haloalkanes) (ii) Alkenyl halides (haloalkenes) (iii) Aryl halides (haloarenes). Compounds in which the halogen atom is bonded to an alkyl or a substituted alkyl-group are called **alkyl halides.** Compounds in which a halogen atom is attached to a carbon atom which is attached to another carbon atom by a double bond are called **alkenyl** (vinylic or vinyl) **halides.** Finally, compounds in which one of the hydrogen of an aromatic ring is replaced by a halogen atom are called **aryl halides.** A few examples are given below:

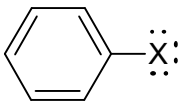


A haloalkane (an alkyl halide)

A haloalkene (an alkenyl or vinylic halide)



A Haloalkyne

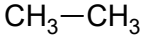


A haloarene (an aryl halide)

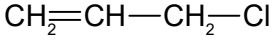
In polyfunctional compounds, where groups other than halogen functional groups are present, one group is identified as the principal functional group and this principal functional group is used as a suffix in the name of the compound. The priorities for selection of principal functional group are given below in the order of decreasing precedence: carboxylic acid, sulphonic acid, ester, acid anhydride, acylhalide, amide, nitrile, aldehyde, ketone, alcohol, thiol, amine, imine, alkyne, alkene, ethers, halides, nitro. Notice the IUPAC name of allyl chloride in main text.

Before going further in details of classification of alkyl halides, just to recall, in IUPAC system of nomenclature, a halo- (i.e. fluro-, chloro-, bromo-, or iodo-) is prefixed and the carbon chain is so numbered so as to give the lowest number to the carbon to which the halogen is attached. When more than one of halogen atoms are present, their names are arranged in alphabetical order. Common names are arrived at by writing the name of alkyl group followed by the name of the halide.

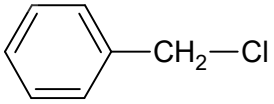
Alkyl halides are further classified on the basis of nature of carbon atom [i.e. primary (1°), $RCH_2{-}X$; secondary (2°), $R_2CH{-}X$ or tertiary (3°), $R_3C{-}X$] and on the basis of number of halogen atoms present in a molecule [i.e. mono-, di-, tri- or tetra-). Now we will consider few examples of simple alkyl halides from each class (name given in brackets are common names):



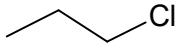
Bromomethane (Methyl bromide)



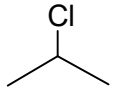
3-Chloropropene (Allyl chloride)



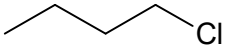
Chloromethylbenzene (Benzyl chloride)



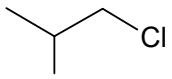
1-Chloropropane (*n*-Propyl chloride) (1°)



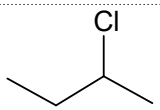
2-Chlropropane Isopropyl chloride) (2°)



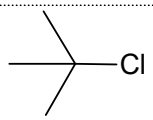
1-Chlorobutane (*n*-Butyl chloride) (1°)



1-Chloro-2-methypropane
(Isobutyl chloride)
(1^o)



2-Chlorobutane
(*sec*-Butyl chloride)
(2^o)



2-chloro-2-methylpropane
(*tert*-Butyl chloride)
(3^o)

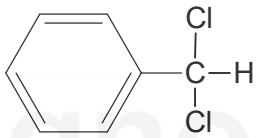
Di-, tri-, and tetrachloromethanes are examples of di-, tri-, and tetra halogen derivatives, respectively,

CH_2Cl_2	$CHCl_3$	CCl_4
Dichloromethane (Methylene chloride)	**Trichloromethane** (Chloroform)	**Tetrachloromethane** (Carbon tetrachloride)

These halogen derivatives are excellent solvents for nonpolar and slightly polar substances.

The dihalogen derivatives of alkyl halides can be subdivided into two types:

i) **Geminaldihalides:** In these both halogen atoms are attached to the same carbon atom i.e., they are in geminal (gem-) position. Geminaldihalides are also referred to as alkylidene halides.

$CH_3CH_2CHCl_2$	$CH_3CBr_2CH_3$	
1,1-Dichloroethane (Ethylidene chloride)	**2,2-Dibromopropane** (Isopropylidenedibromide)	**Dichloromethylbenzene** (Bezyylidine chloride or benzal chloride

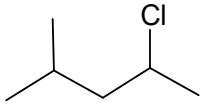
ii) Vicinal dihalides: When two halogen atoms are attached to adjacent carbon atoms, they are said to be in **vicinal (vic-)** position and such compounds are also named as the dihalides.of the alkene from which they may be prepared by addition of the halogen, e.g.

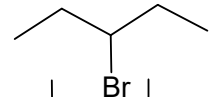
CH_2BrCH_2Br	$CH_3CHClCH_2Cl$
1, 2-Dibromoethane1 (Ethylene dibromide)	**2-Dichloropropane** (Propylene dichloride)

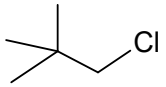
We have discussed above classification of halogen derivatives. In the next section, we shall be discussing the preparations of mono halogen derivatives of alkyl halides and alkenyl halides. We will take up aryl halides separately in next unit. Before that, try the following SAQ to test your understanding of the classification of halogen derivatives.

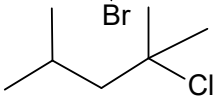
SAQ 1

Classify each of the following alkyl halides as 1°, 2°, or 3°.Also write IUPAC name of each compound.

a) 

b) 

c) 

d) 

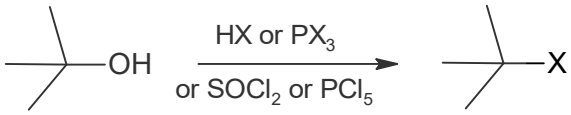
13.3 PREPARATION OF ALKYL HALIDES

We have already looked at several methods of preparation of halogen derivatives in earlier units of 1st semester course. In this section, we shall briefly review these methods and also take up some other methods for the preparation of halogen derivatives.

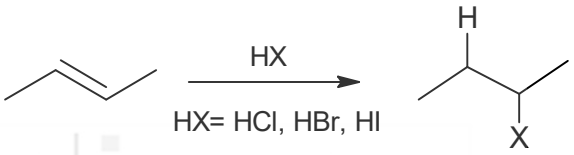
Alkyl halides can be prepared from alcohols, alkenes, alkanes, Grignard reagents, carboxylic acids, other halides and by chloromethylation of benzene. General reactions of these methods of preparation are summarised below in Table 13.1.

Table 13.1: Preparation of alkyl halides

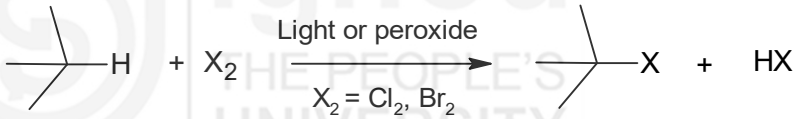
From Alcohols



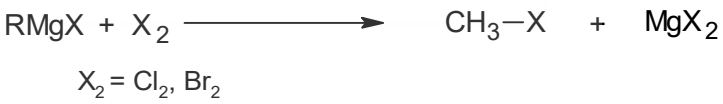
From Alkenes



From Alkanes



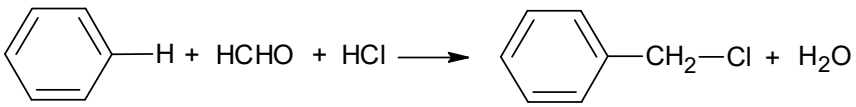
From Grignard Reagents



From Carboxylic Acids

From Halide Exchange

From Chloromethylation of Benzene



Let us study these methods of preparation in a brief manner.

i) **From alcohols:** The most widely used method for the preparation of alkyl halides is from alcohols. The hydroxyl group of the alcohol (R—OH) can be replaced by a halogen atom by using either a hydrogen halide (HX), a phosphorus halide (PX_3 or PCl_5), or thionyl chloride ($SOCl_2$). These reactions

will be discussed in more detail in the next unit. The net reaction is represented by the equations,

$$R—OH + HX \rightarrow R—X + H_2O$$

$$R—OH + PCl_3 \rightarrow R—X + H_3PO_3$$

$$R—OH + PCl_5 \rightarrow R—Cl + POCl_3 + HCl$$

$$R—OH + SOCl_2 \rightarrow R—Cl + SO_2\uparrow + HCl$$

$$C_6H_5CH_2—OH + SOCl_2 \longrightarrow CH_3CH_2—Cl$$

Phenylmethanol (Benzyl alcohol) — **Chloromethylbenzene** (Benzyl chloride)

ii) From alkenes: Hydrogen halides (HCl, HBr, HI) reacts with alkenes to form alkyl halides. The mode of addition follows Markownikoff's rule except for the addition of hydrogen bromide in the presence of peroxide. The mechanisms for both modes of additions were shown in Unit 17 of first semester course.

Examples:

$$CH_3—CH=CH_2 + HCl \longrightarrow CH_3—\underset{Cl}{CH}—\underset{H}{CH_2}$$

1-Propene → **2-Chloropropane**

$$CH_3—CH=CH_2 + HBr \longrightarrow CH_3—\underset{Br}{CH}—\underset{H}{CH_2}$$

2-Bromopropane

$$CH_3—CH=CH_2 + HBr \xrightarrow{\text{Peroxide}} CH_3—\underset{Br}{CH}—\underset{H}{CH_2}$$

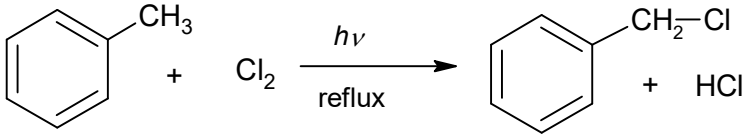
1-Bromopropane

iii) From Alkanes: Direct halogenation of alkanes is of limited application because in most cases mixture of mono and polyhalogenated compounds is formed. You have learned in Unit 17 that chloromethane, however, can be prepared directly by photochlorination or heating if a large excess of methane is employed. Similarly tetrachloromethane (carbontetrachloride), CCl_4, can also be prepared from methane if a large excess of chlorine is used.

$$CH_4 + Cl_2 \xrightarrow[\text{Excess of methane}]{\text{Sun light}/\Delta} CH_3Cl$$

$$CH_4 + Cl_2 \xrightarrow[\text{Excess of chlorine}]{\text{Sun light}/\Delta} CCl_4$$

Chloromethylbenzene can also be similarly prepared.

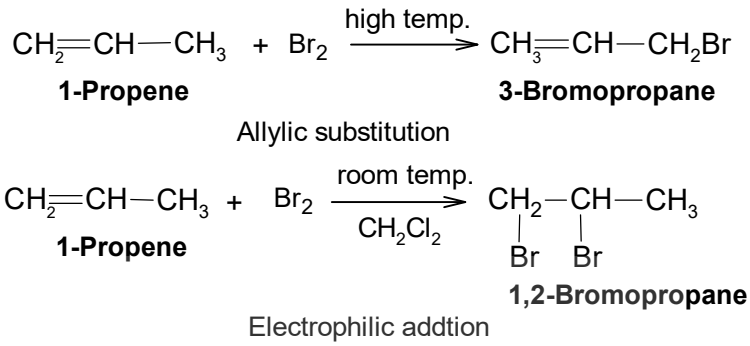


Methylbenzene (Toluene) — **Chloromethylbenzene** (Benzyl chloride)

Allylic carbon: A carbon adjacent to a carbon-carbon double bond.

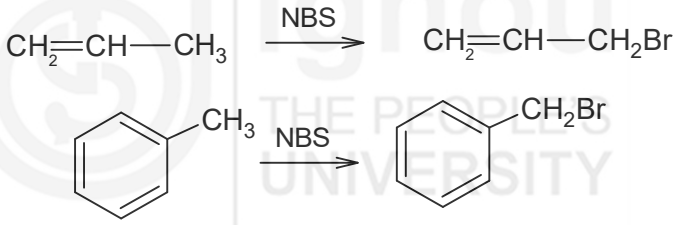
Selectivity in allylic substitution is due to the resonance stability of intermediate allylic radical.

The above mentioned reactions are examples of free radical substitution reactions. Alkenes having allylic carbon undergo similar type of reactions at high temperature or in the presence of light rather usual electrophilic addition reactions. Such reactions are called allylic substitution.

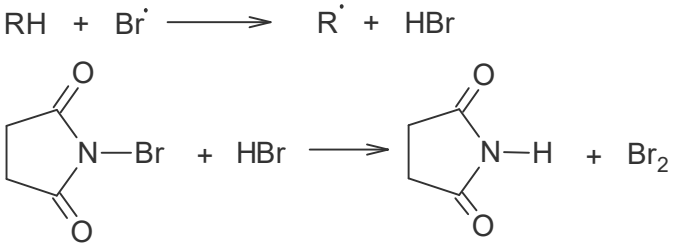


This is because in the first reaction above, the formation of π-complex which is an intermediate in halogen addition reaction, unfavourable in the absence of polar solvent. Therefore, substitution is favoured over addition. At high temperature concentration of halogen radicals is much higher than at room temperature, which further accelerates substitution.

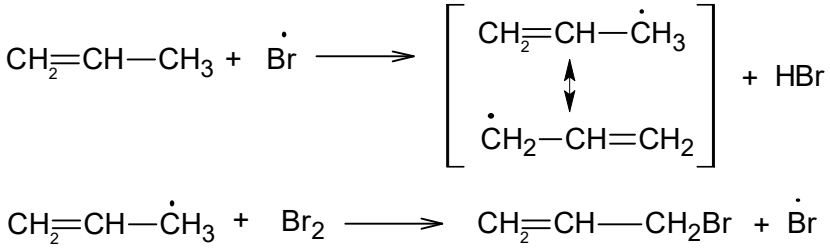
N-Bromosuccinimide (NBS) deserves a special mention because it is a specific reagent for bromination at allylic and benzylic positions in alkenes.



A mechanism has been proposed for such reactions, in which NBS acts as a bromine reservoir maintaining a low concentration of molecular bromine by reacting with HBr, which is initially formed in a side reaction:



Bromine molecule dissociates into bromine atoms on heating or on exposed to light. Radical bromine abstracts hydrogen from allylic position and generates resonance stabilised allylicradical which then reacts with molecular bromine to give the product.



The chain then continues with the production of HBr and bromine atoms. A low concentration of bromine favours allylic bromination over addition to the double bond.

iv) **From Grignard reagents:** Direct reaction of alkyl or aryl halides with metallic magnesium in a dry solvent (ether) gives the Grignard reagent, a valuable intermediate in synthetic organic chemistry. Grignard reagents react with halogens to give alkyl halides.

$$RMgX + X_2 \longrightarrow R{-}X + MgX_2$$

Grignard Reagent — Alkyl halide

v) **From carboxylic adds:** The dry silver salt of a carboxylic acid upon refluxing with bromine in tetrachlomethane (carbon tetrachloride) affords the corresponding alkyl bromide. This reaction is known as **Hunsdiecker reaction.**

$$RCOOAg + Br_2 \longrightarrow R{-}Br + AgBr + CO_2\uparrow$$

Silver salt of carboxylic acid

vi) From Halide exchange: This is a good procedure for preparing alkyl iodides and alkyl fluorides.

$$R{-}X + KI \xrightarrow{\text{acetone}} R{-}I + KX$$

Alkyl fluorides often are prepared by the reaction of metallic fluoride such as AgF, Hg_2F_2, CoF_2 or SbF_3. The reaction is termed as **Swarts** reaction.

$$2R{-}Cl + Hg_2F_2 \longrightarrow 2R{-}F + Hg_2Cl_2$$

Alkyl Chloridefluoride — **Mercurous fluoride** — **Alkyl chloride** — **Mercurous**

$$3CCl_4 + SbF_3 \longrightarrow 3CCl_2F_2 + 2SbCl_3$$

Tetra-Chloromethane — **Antimony fluoride** — **Dichloro-fluorometane**(Freon12) (a chlorofluorocarbon, CFC)

Chlorofluorocarbons (CFC) also called Freons are inert nontoxic gases used as refrigerants in air— conditioners and refrigerators. Freon 12 is the most commonly used refrigerant. Unfortunately Freons catalyse the decomposition of ozone and thus can destroy the protective layer that surrounds the earth. For this reason most of countries in the world have banned the use of Freons.

vii) From Chloromethylation of benzene: This method isused to prepare benzylic halides.

$$Ar{-}H + CH_2O + HCl \longrightarrow Ar{-}CH_2{-}Cl + H_2O$$

Aromatic Hydrocarbon — **Methanal** (Formaldehyde) — **Benzylic halide**

SAQ 2

Write equations showing the preparation of the following halides from the starting materials indicated.

a) $C_6H_5CHBrCH_3$ from $C_6H_5CH_2CH_3$

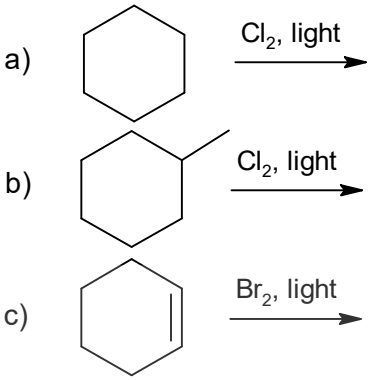
b) $CH_3CHBrCH_3$ from $CH_3CHOHCH_3$

c) 1-bromopropane from propene

d) 1,2-dibromopropane from propene

SAQ 3

Predict the monohalogenation product that might be formed in the following reactions.



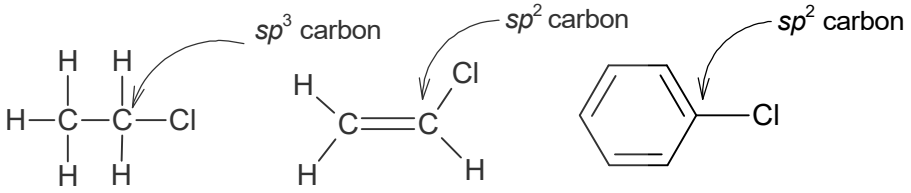
13.4 STRUCTURE AND PROPERTIES OF HALOGEN DERIVATIVES

In the previous section, we have discussed the preparation of alkyl halides. Now we will discuss to the structure and physical properties of halogen derivatives along with chemical properties of allkyl halides.

13.4.1 Structure of Halogen Derivatives

In a halogen derivative, halogen atom is the functional group, and the C−X bond is the site of chemical reactivity. As might be expected, the nature of the chemical bond between the halogen and carbon decides the reactivity of halogen derivatives.

In the alkyl halide, the carbon-halogen sigma bond results through overlap of the sp^3 hybrid orbital with the *p* orbital of the halogen atom. The carbon halogen sigma bond in alkenyl and aryl halides results from the overlap of sp^2 hybrid orbital of the carbon with a halogen *p* orbital.



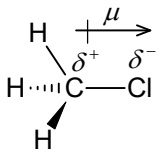
As you know, the bond formed by halogen with a sp^2 hybridised carbon is shorter and stronger than the bond formed with a sp^3 hybridised carbon because of the higher *s* character. This difference in the nature of the C−X bond is mainly responsible for different behaviour of aryl and alkenyl halides as compared to alkyl halides. To further explain the unique chemistry of aryl and alkenyl halides, we shall study the reactions of chlorobenzene and chloroethene in next unit. Let us first examine the nature of the C−X bond in alkyl halides.

Electronegativity on the Pauling and Sanderson scales

Element	Pauling	Sanderson
F	4.0	4.000
Cl	3.0	3.475
Bi	2.8	3.219
I	2.5	2.778
C	2.5	2.746

You may recall that halogens are more electronegative than carbon and thus the C−X bond of alkyl halide is polarised and the electron density along the C−X bond increases in the direction of X. This effect places a partial negative charge (δ^-) on the halogen atom and a partial positive charge (δ^+) on the carbon atom. The

resulting dipole moment is appreciable and governs a substantial part of the chemical and physical properties of the halogen derivatives.



The magnitude of dipole moment depends on the electronagativities of the bonded atoms. For methyl halides, dipole moment is summarised in Table 13.2.

The dipole moment (μ) is a measure of the polarity of the molecule. It is the product of charge (e) and distance (d).

$$\mu = e \times d$$

Table 13.2 : Dipole Moments of Methyl Halides

Compound	Dipole moment μ, D (C m)
CH_3F	6.16×10^{-30} (1.85 D*)
CH_3Cl	6.23×10^{-30} (1.87 D)
CH_3Br	6.03×10^{-30} (1.81 D)
CH_3I	5.40×10^{-30} (1.62 D)

***Where D is debye unit, 1 D = 3.33 x 10^{-30} C m (Coulomb/meter)**

Another important factor on which the nature of C−X bond depends is its bond strength. Bond enthalpies, which measure the bond strength, decrease as we go down the group in the periodic table. This is because, the size of halogen atom increases as we go down the group in the periodic table, fluorine atom is the smallest and iodine atom, the largest. Consequently the carbon-halogen bond length also increases from C−F to C−I and bond strength decreases from C−F to C−I. Bond lengths and bond enthalpies of typical halides are given in Table 13.3. These bond energy values show that C−I bond is the weakest bond and C−F bond is the strongest bond. Therefore, the order of reactivity of haloalkanes is iodoalkane > bromoalkane > chloroalkane > fluoroalkane. We will further go in details of the relative reactivity of alkyl halides in subsequent sections. We will also explain how the slight positive charge on the carbon attached to halogen atom is mainly responsible for the nucleophilic substitution (S_N) reactions of halogen derivatives.

Table 13.3: Carbon-Halogen (C−X) Bond Length and BondEnthalpies

Bond	Bond length/pm	C-X Bond enthalpy/ kJ mol^{-1}
C—F	139	452
C—Cl	178	351
C—Br	193	293
C—I	214	234

Thus we can summarise that **both dipole moment and bond strength of C−X govern a substantial part of the chemical and physical properties of the halogen derivatives.**

13.4.2 Physical Properties of Halogen Derivatives

The alkyl halide has a higher boiling point than an alkane of comparable size and shape. For example, the boiling points of ethane and bromomethane are 184 K and 277.5 K, respectively. Although both the molecules are approximately of same size. The boiling point of bromethane is considerably higher. This difference in boiling point is due to the dipole moment in bormomethane. The dipole-dipole interactions increase van der Waals forces among molecules; therefore, more energy is needed to overcome these forces before boiling. The physical properties such as boiling points and densities of some alkyl halides, aryl halides and alkenyl halides are summarised in Table 13.3. Common names of some of them are also given.

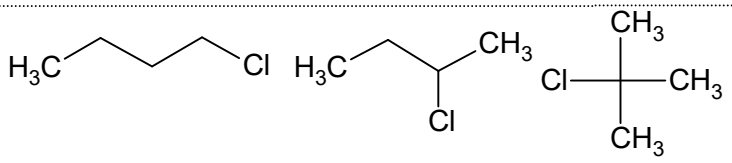
Van der Waals forces: A group of intermolecular attractive forces including dipole-dipole, dipole-induced dipole, and induced dipole-induced dipole forces. These forces are very week in comparison to electrostatic ionic forces in ionic compounds.

Table 13.3: Physical properties of halogen derivatives

IUPAC Name	Common Name	Formula	Bp,K	Density, kg dm^{-3} at b293 K
Alkyl halides				
Fluoromethane	Methylfluoride	CH_3F	195	Gas
Chloromethane	Methylchloride	CH_3Cl	249	Gas
Bromomethane	Methybromide	CH_3Br	277.5	Gas
Iodomethane	Methyliodide	CH_3I	315.8	2.28
Dichloromethane	Methylene chloride	CH_2Cl_2	313	1.34
Trichloromethane	Chloroform	$CHCl_3$	334	1.49
Tetrachloromethane	Carbontetrachloride	CCl_4,	350	1.60
Aryl halides				
Fluorobenzene	—	C_6H_5F	358	1.024
Chlorobenzene	—	C_6H_5Cl	405	1.107
Bromobenzene	—	C_6H_5Br	429	1.495
Iodobenzene	—	C_6H_5I	462	1.832
Alkenyl halides				
Chloroethene	Vinyl chloride	CH_2=CHCl	259	Gas

Note the increase in boiling point and density with the increase in the atomic mass and atomic size of the halogens atom. The table emphasises also the increase in the boiling point with the progressive replacement of the hydrogen atoms with halogen atoms. These effects are related to the enhancement of van der Waal's attraction with the increase in molecular volume. Compare, for example, the boiling points of CH_3Cl, CH_2Cl_2, $CHCl_3$, and CCl_4. The density would also increase in the same way.

The boiling points of higher alkyl halides increase with the increase in mass and size. Boiling points of isomeric alkyl halides decrease with increase in branching. For example, 2-chloro-2-methylpropane has the lowest boiling point among the three isomers.



Bp = 350.5 K Bp = 341.7 Bp = 324.5

In general, halogen compounds are insoluble in water but are readily soluble in organic solvents and with the exception of some fluro and mono-chloro compounds, they are more dense than water. Aryl halides are fairly pleasant smelling liquids, but benzylic halides having the structure $ArCH_2X$ are irritating to the eyes, skin and nasal passage. The toxicity varies. However, the polychlorinated hydrocarbons such as CCl_4 and $CHCl_2CHCl_2$ are quite toxic and should be used with care.

SAQ 4

Arrange the following molecules in order of increasing boiling points. Give reason for this trend.

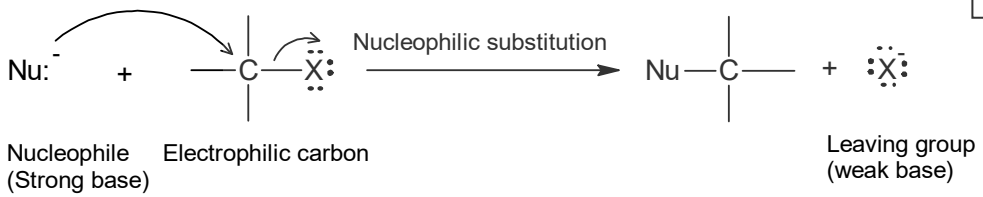
$CHCl_3$, CH_2Cl_2, CCl_4, CH_3Cl

13.4.3 Chemical Properties of Alkyl Halides

Most important reactions of alkyl halides are **nucleophilic substitution (S_N)** and **elimination** (E). In this section we shall take up a fairly detailed description of these reactions. We have already encountered the term nucleophilic reagent or nucleophile and have learned that it is applied to an electron rich atom or group such as,

1) **Substitution reactions:** As explained earlier the C−X bond is polar bond, and the carbon to which halogen group is attached carries a positive charge because of the higher electronegativity of halogens compared to carbon. The carbon atom is, therefore, susceptible to attack by a nucleophile.

Nucleophilic substitution refers to a reaction in which an electron-rich nucleophile, $Nu:^-$, replaces a leaving group, X^-.



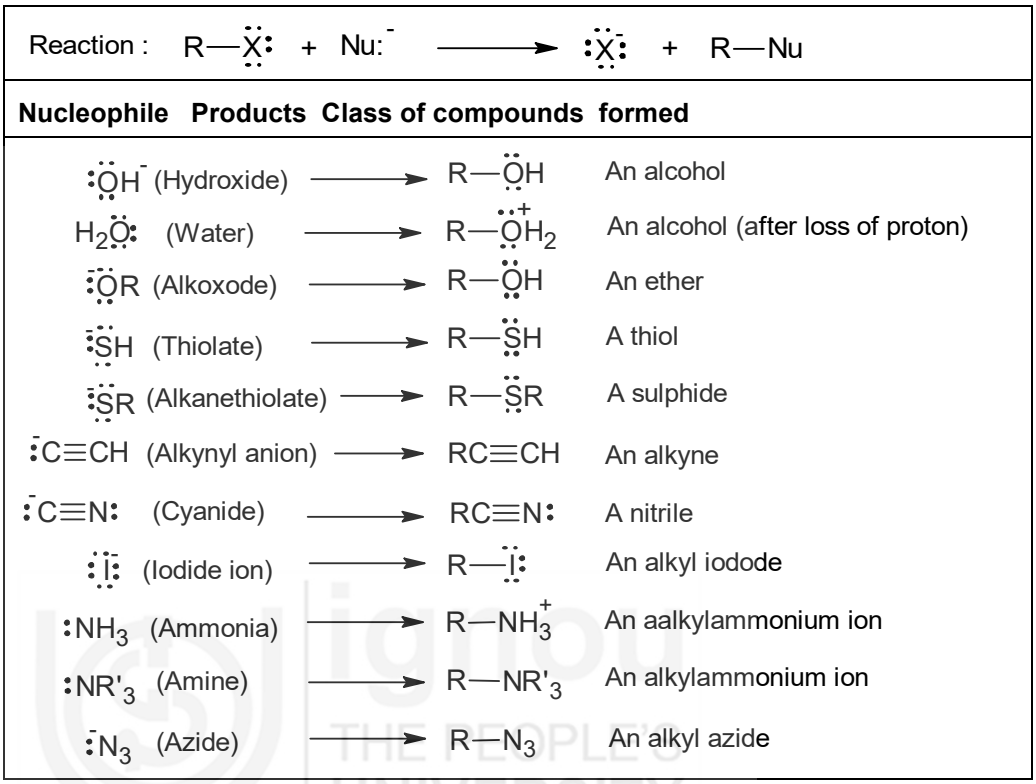
If we regard the reaction as a type of Lewis acid-base reaction, then we can understand that it tends to occur because of the formation of the halide ion which, as the conjugate base of a strong acid (HX), would be a weak base. Accordingly, a weak base like the halide ion is said to be a good **leaving group.** The order of reactivity of the alkyl halides increases from fluoro-substituted to iodo-substituted compounds

RF < RCl < RBr < RI

The reason of this order is that the iodide ion, being the weakest base as the conjugate base of the strongest acid, HI, is the best leaving group, the fluoride ion being a stronger base is the poor leaving group.

Now let us summarise some nucleophilic substitution reactions of alkyl halides in Table13.4.

Table 13.4: Some Nucleophilic Substitution Reactions



On the basis of the mechanism of substitution reactions, nucleophilic substitution reaction can be divided into two types:

i) S_N2 reactions (S_N2 means 'substitution, nucleophilic bimolecular')

ii) S_N1 reactions (S_N1 means 'substitution, nucleophilic unimolecular')

The terms bimolecular and unimolecular are related to the number of molecules involved in the rate determining step in these reactions. Now, let us consider these reactions in detail.

The S_N2 reaction: The reaction of bromoethane with the hydroxide ion to yield ethanol and bromide ion is a typical example of S_N2 reaction.

$$CH_3CH_2{-}Br + OH^- \longrightarrow CH_3CH_2{-}OH + Br^-$$

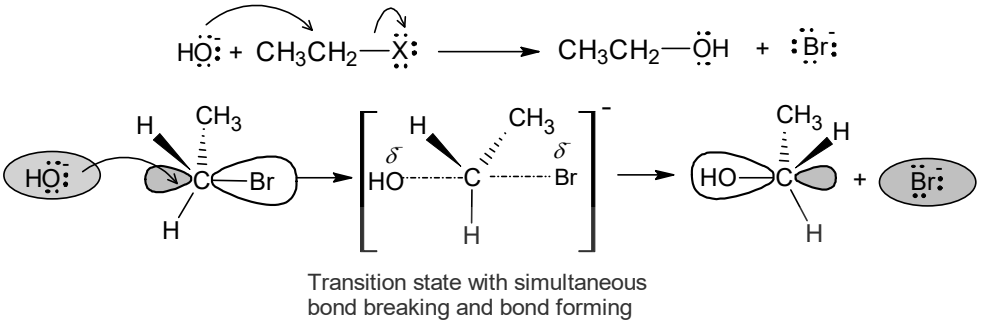
Bromoethane **Ethanol**

In general methyl or primary alkyl halides undergo S_N2 reaction with any relatively strong nucleophile: OH^-, OR^-, CN^- etc. Secondary alkyl halides can also undergo S_N2 reactions, but, tertiary alkyl halides do not. The above reaction has been found to follow second order kinetics which means that the rate of the reaction is proportional to the concentrations of both the alkyl halide and the hydroxide ion. Thus, for the above reaction,

$$\text{Rate} = k_2[C_2H_5Br]\,[OH^-]$$

Where k_2 is the rate constant and $[C_2H_5Br]$ and $[OH^-]$ represent the concentrations in mole dm^{-3} of the alkyl halide and the hydroxide ion, respectively.

Mechanism: On the basis of reaction kinetics and the stereochemistry of S_N2 reactions, a one step, concerted mechanism is proposed.



Transition state with simultaneous bond breaking and bond forming

Fig. 13.1: The mechanism for S_N2 reaction. The dashed lines are depicting partially formed or broken bonds.

In an S_N2 reaction, the other three bonds, (which are not taking part in substitution change) to the central carbon progressively flatten put and flip to the other side of the carbon in a manner similar to the spokes of an umbrella inverting in a windstorm. The flipping is called inversion of configuration, or Walden inversion, which you have already studied in Unit 3.

Note how the hydroxide ion attacks from the rear, away from the negatively charged field of the bromide ion. As the hydroxide ion begins to bond to the carbon atom from the rear, the bromine begins to leave as the bromide ion from the front. Groups larger than hydrogen tend to block the approach of the nucleophile, so methyl halides are more reactive than other primary halides. Table 13.5 shows the effect of the structure of alkyl halides over the reaction rate. In this table we have given average reaction rates (taking the reaction rate for ethyl halides are one) of S_N2 reaction of some alkyl halides.

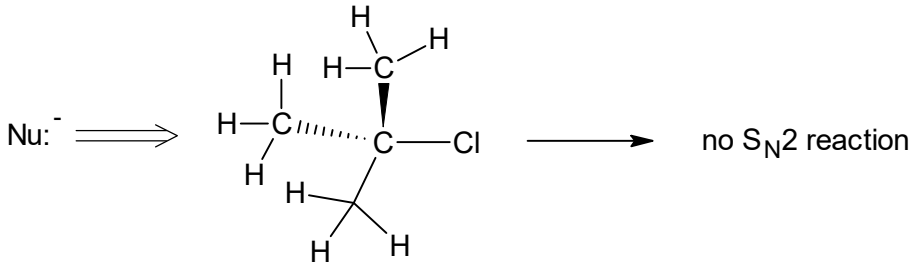
Table 13.5: Effect of branching in the alkyl hallde on the rate of S_N2 reaction

Alkyl halide	Reaction rate
CH_3-X	30
CH_3CH_2-X	1
$(CH_3)_2CH-X$	0.02
$(CH_3)_3C-X$	0

Therefore, among alkyl halides, order of relative rate is

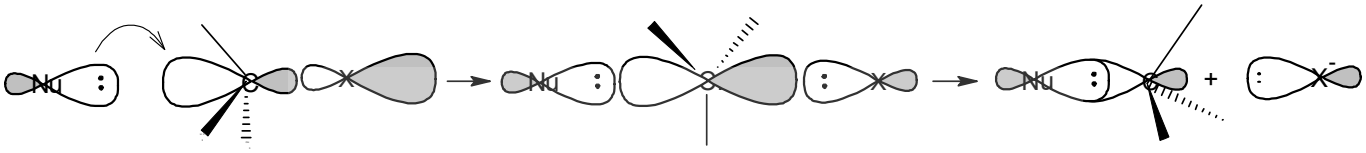
CH_3 > *p*-RX > *sec*-RX > *tert*-RX

This order of reactivity is interpreted to be due to steric hindrance, which means obstruction of space. The more the number of alkyl groups around the carbon holding the halogen, the more they hinder the nucleophile approaching at backside of that carbon.



***tert*-Butyl bromide**

Molecular orbital model provides a good description of the bonding interactions that occur in the S_N2 process. The filled nonbonding orbital of nucleophile is attacking from the backside of the antibonding molecular orbital, σ^*, of the C−X bond, weakening the C−X bond as the new C−Nu, σ bond becomes stronger. The back side interaction of nucleophile is the most effective way to fill this nonbonding, σ^* orbital, which result in breaking of the C−X bond. Thus both valance bond and molecular orbital models predict that the S_N2 reaction proceeds through a transition state with the inversion of the configuration.



Antibomding (σ*) C-Cl orbital Transition state

In the transition state, the hybridisation of the central carbon atom changes from sp^3 to sp^2. The geometry of the transition state is trigonal bipyramidal with one bond partially forming and one bond partially breaking. Finally, sp^3 hybridisation is reestablished in the product with inversion of configuration. The potential energy diagram of S_N2 reaction is given in Fig. 13.2, which illustrates potential energy change during the formation of substituted product.

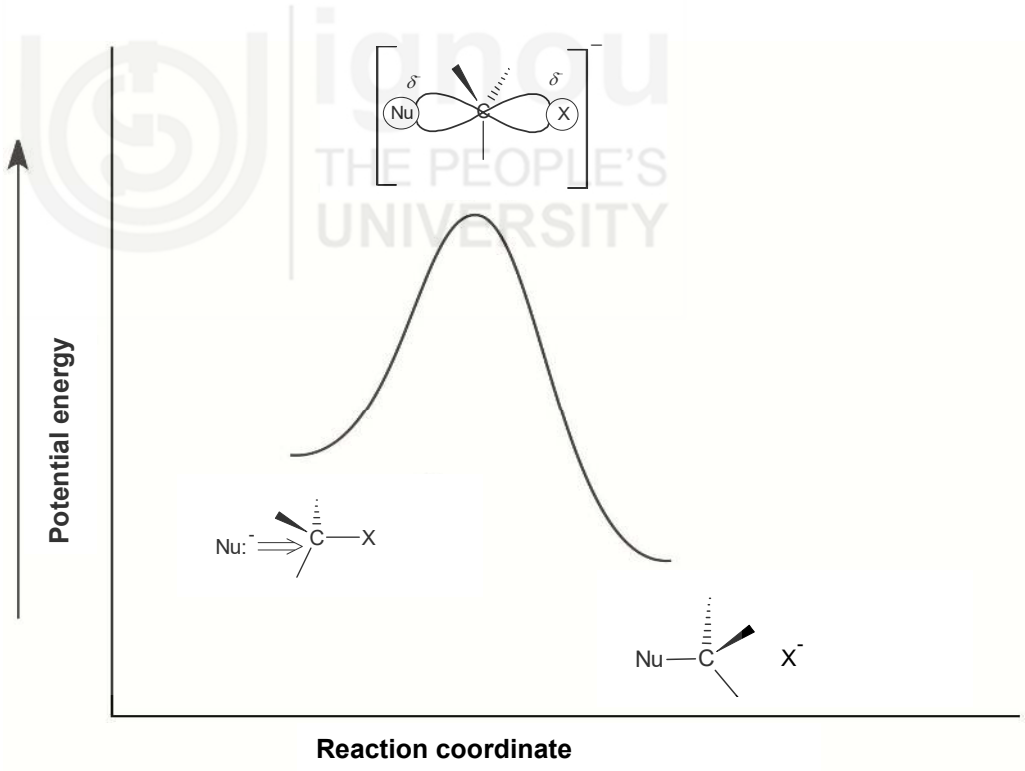


Fig. 13.2: **Potential energy diagramed for the S_N2 reaction. Higher energy state indicates transition state.**

The S_N1 reaction:

You can see from Table 13.5, that the tertiary alkyl halides do not undergo S_N2 reaction. And yet when tertiary butyl bromide is treated even with a very weak base, (such as H_2O or CH_3CH_2OH) substitution takes place. Now, the question arises, if tertiary alkyl halides cannot undergo S_N2 reaction, how are the

substitution products formed? The answer is that tertiary alkyl halides undergo substitution by a different mechanism, called the S_N1 reaction (substitution, nucleophilic, unimolecular). An example of such a reaction is the hydrolysis of 2-chloro-2-methylpropane with water. This reaction is found to be of first order (S_N1). That means the rate of the reaction is proportional to the concentration of the one reacting species i.e. alkyl halide and independent of the concentration of the nucleophile.

$$\text{Rate} = k_1 [(CH_3)_3CCl]$$

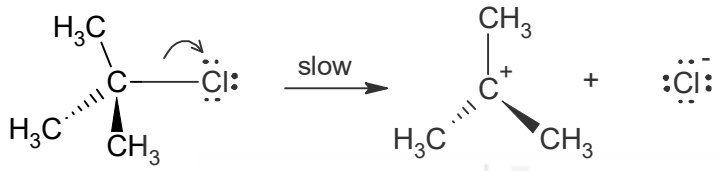
In this equation, k_1 represents the first order rate constant and $[(CH_3)_3CCl]$ represents the concentration of the alkyl halide in mole dm^{-3}.

Mechanism: On the basis of reaction kinetics and stereochemistry of S_N1 reaction, a two steps mechanism has been proposed for this reaction.

Nucleophiles such as H_2O or CH_3CH_2OH are also used as the solvents. Substitution reactions of such nucleophiles are sometime called solvolysis reactions (from solvent and by "breaking down" or "loosing").

In most stepwise reactions, the slowest step in the entire sequence is the rate-determining step as a reaction cannot proceed faster than its slowest step does.

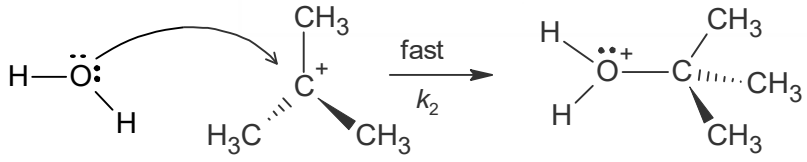
Step 1: Ionisation ofthe C−X bond forms a carbocation intermediate. This is the relatively slow, rate determining step.



2-Chloro-2-methylpropane
(*tert*-Butyl chloride)

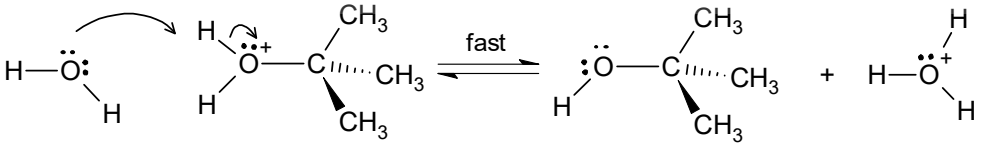
Carbocation intermediate

Step 2: Carbocation (an electrophile) reacts with water (a nucleophile) to form an oxonium ion.



Nucleophile Electophile An oxonium ion

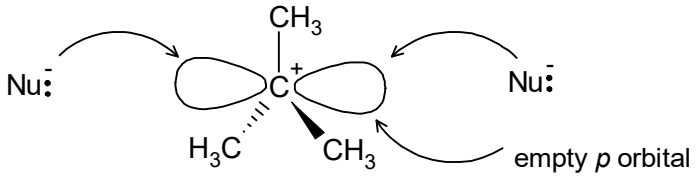
Proton transfer from the oxonium ion to water completes the reaction and gives 2-methyl-2-propanol (*tert*-butyl alcohol)



2-Methyl-2-propanol
(*tert*-Butyl alcohol)

From the above mechanism it is clear that the first step in this mechanism is ionisation of the alkyl halide to a carbocation intermediate. This ionisation is a simple heterolytic bond cleavage. In the second step, a nucleophile may approach the central carbon atom from either side with equal probability

(unlike the S_N2 reaction where the nucleophile approaches only from the back). According to valance bond approach, the central carbon atom of carbocation is sp^2 hybridised and it has a trigonal planar geometry and, therefore, the nucleophile may engage the empty *p* orbital from either side of the molecule.



Thus, S_N1 reaction of an optically active alkyl halide should give racemic substitution products. The potential energy diagram of S_N1 reaction is given in Fig. 13.3. Step 1 has high energy of activation and is, therefore, the slow step. As shown in this figure, an intermediate carbocation has lower energy than transition states shown as I and II where bond breaking and bond making actually occur.

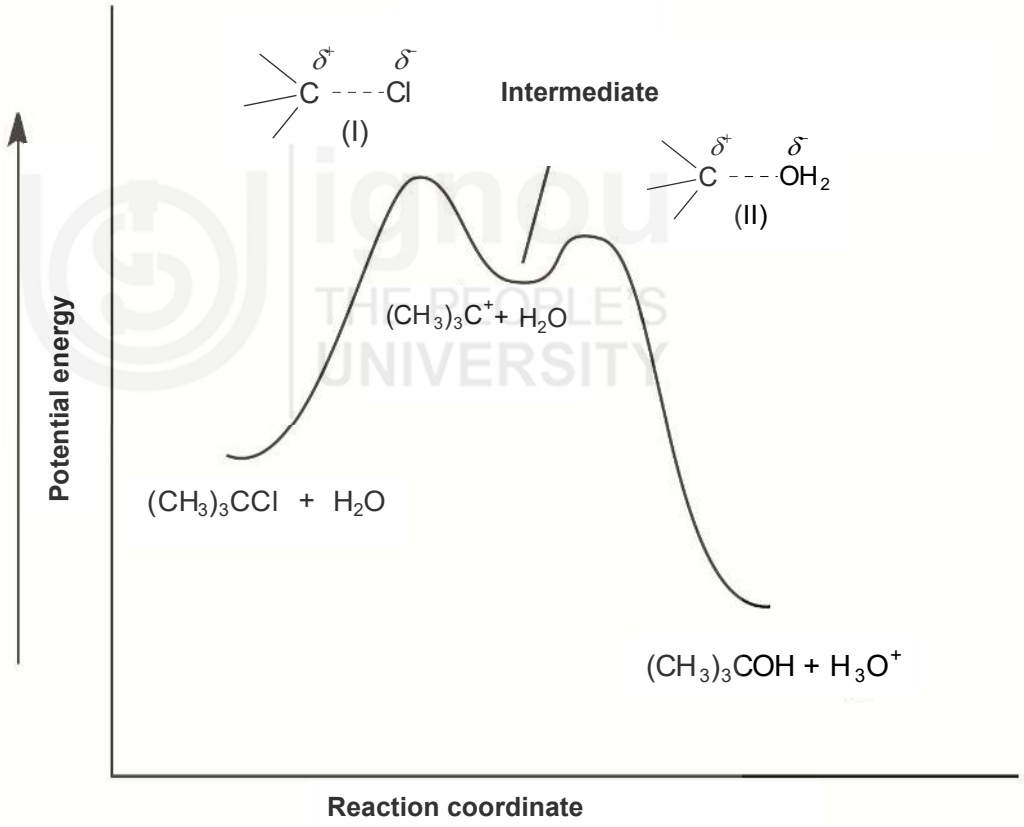


Fig. 13.3: Potential energy diagram for hydrolysis of 2-chloro-2-methylpropane by S_N1 mechanism. You can see two transition states. The first (I) is for formation of the carboction intermediate, the second (II) is for the reaction of the carbocation with nucleophile (H_2O) to give an oxonium ion.

As in the case of S_N2 reaction, the structure of the alkyl halides also affects the rate of the reaction. We are giving the relative rates of reaction of some alkyl bromides under typical S_N1 conditions in Table 13.6.

Table 13.6: Relative reaction rates of hydrolysis of some alkyl bromides under typical S_N1 conditions

Alkyl bromide	Relative rate
CH_3-Br	1.00*
CH_3CH_2-Br	1.00*
$(CH_3)_2CH-Br$	11.6
$(CH_3)_3C-Br$	1.2×10^6

*The observed reactions on the methyl or other primary alkyl bromides probably occur by S_N2 route not S_N1 so their relative rates are considered as one.

Therefore, among alkyl halides, the order of relative rates is

tert-RX>*sec*-RX >*p*-RX > CH_3X

This order is reasonable, since the order of stability of the intermediate carbocation formed in the slow rate determining step is also the same.

$(CH_3)_3C^+ > (CH_3)_2CH^+ > CH_3CH_2^+ > CH_3^+$

Tertiary Secondary Primary

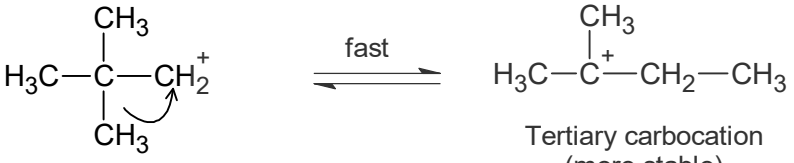
The S_N1 reaction has also been found to be associated with rearrangements. The intermediate carbocation can rearrange to a more stable carbocation. The following is an example of one such rearrangement:

Step 1

1-Bromo-2,2-dimethylpropane
(Neopentyl bromide)

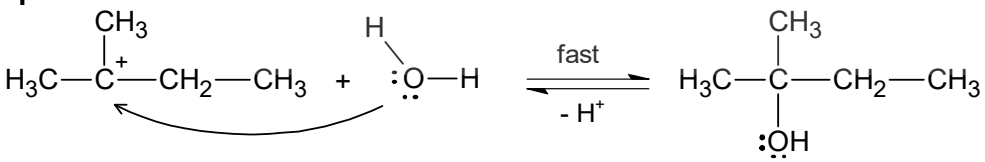
Primary carbocation
(less stable)

Step 2



Tertiary carbocation
(more stable)

Step 3



2-Methyl-2-butanol
(*tert*-Amyl alcohol)

You can notice in step 2, how the primary carbocation rearranges, through the shift of a —CH_3 group, to produce the more stable tertiary carbocation.

After studying both the mechanisms, you can point out some of key differences. First, S_N2 reaction involves a single step and has no intermediate. In contrast, S_N1 reaction has two steps with the formation of intermediate

Among halide ions, iodide anion is having the largest size and is least electronegative, its negative charge is delocalised over the large volume of space, therefore, is the most stable. Thus, HI is the strongest acid of halogen acids. On the other hand, fluoride anion is the smallest ion, its charge is the most concentrated, and fluoride ion is the least stable. Therefore, it is the weakest acid of the halogen acids.

carbocation. S_N2 follows second order kinetics whereas S_N1 follows first order kinetics. S_N2 reaction of an optically active alkyl halide gives product with inversion of the configuration, on the other hand,S_N1 reaction of an optically active alkyl halide gives generally racemic substitution products. In S_N2 reaction, each replacement of hydrogen by an alkyl group decreases the rate of reaction and opposite is observed in S_N1 reaction. Nature of halide group also influences the rate of reaction. We have seen in transition state of both S_N2 and S_N1 reactions that the leaving group develops a partial negative charge. Therefore, the ability of a leaving group is related to how stable it is as anion. The most stable anions are the best leaving group and the weak conjugate bases of strong acids. Thus on the basis of strength of acids we can determine which anion is best leaving group. For example the order of relative strength of halogen acids and relative stability of halide ions is shown below:

$$\underset{HI}{I^-} > \underset{HBr}{Br^-} > \underset{HCl}{Cl^-} > \underset{HF}{F^-}$$

Stability of anion; strength of acid

Among halogen acids, the order of strength increases from HF(weakest) to HI (strongest). Thus, the best leaving group among halide is I^- and poorest leaving group is F^-.

In fact, both S_N2 and S_N1 mechanisms can be viewed as the limits of a mechanistic continuum. Beside the nature of alkyl halide there are many factors such as nature of nucleophile, nature of leaving group, solvent system used during reaction etc. which influence the preference of one mechanism over the other. We are not going in detail of these factors at this stage but we present a brief overview useful to predict the type of mechanism that dominates under certain reaction conditions in Table 13.7.

Table 13.7: A summary of S_N2 vs S_N1 reactions

Alkyl Halide	**S_N2**	**S_N1**
CH_3-X	S_N2 reaction is favoured	S_N1 reaction does not occur because of the unstable methyl cation
RCH_2-X	S_N2 reaction is favoured	S_N1 reaction rarely occurs as the formation of primary carbocation rarely takes place, exceptions areallylic and benzylic carbocations. Allylic and bebzylic halides follow both S_N2 and S_N1 mechanisms
R_2CH-X	S_N2 reaction is favoured in aprotic solvents with good nucleophile	S_N1 reaction is favoured in protic solvents with poor nucleophiles and good leaving groups
R_3-X Reaction at chiral centre (optically active centre)	S_N2 reaction does not occur because of steric factor. Inversion of the configuration	S_N1 reaction is favoured because of the ease of formation of tertiary carbocation Racemisation is favoured
Rearrangement reactions	No rearrangements in S_N2 reaction	Rearrangements possible during S_N1 reaction

SAQ 5

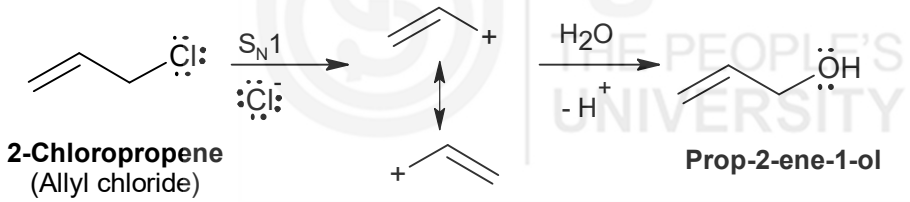
The reaction of 2-bromo-2-methylpropane with azide ion in methanol is a typical S_N1 reaction. What happens to the rate of the reaction if concentration of azide ion is doubled?

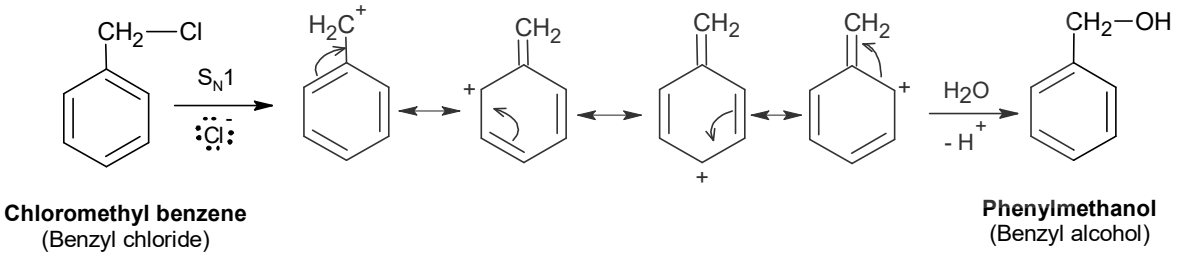
Some Typical Nucleophilic Substitution Reactions:

As mentioned above the mechanism of a particular nucleophilic substitution reaction is based on the structure of alkyl halide, nature of nucleophile and leaving group, and solvent. Now we will consider few reactions which support this argument.

Substitution Reactions of Allylic and Benzylic Halides:

The behaviour of substituted alkyl halides such as allylic and benzylic halides in S_N1 and S_N2 reactions deserves to be considered separately. Both these halides are very reactive under both S_N1 and S_N2 conditions. They undergo S_N1 reaction at faster rate than tertiary alkyl halides. The reason for the enhanced reactivity under S_N1 conditions lies in the **resonance stabilisation** of the carbocation intermediate and for S_N2 reaction in the stabilisation of the S_N2 transition state due to charge delocalisation on π bond orbitals. To illustrate this, further let us consider S_N1 reaction of allyl chloride and benzyl chloride with H_2O.





Now, consider the S_N2 reactions. Allylic halides and benzylic halides also undergo S_N2 reaction at a faster rate than primary alkyl halides or even methyl halides. The reason for the greater S_N2 reactivity of allylic and benzylic halides is stability of the transition state. In the case of allylic and benzylic halides partial overlap of the π bond orbitals helps in delocalisation of the negative charge on the transition structure thus increasing the rate of the reaction (see Fig. 13.4).

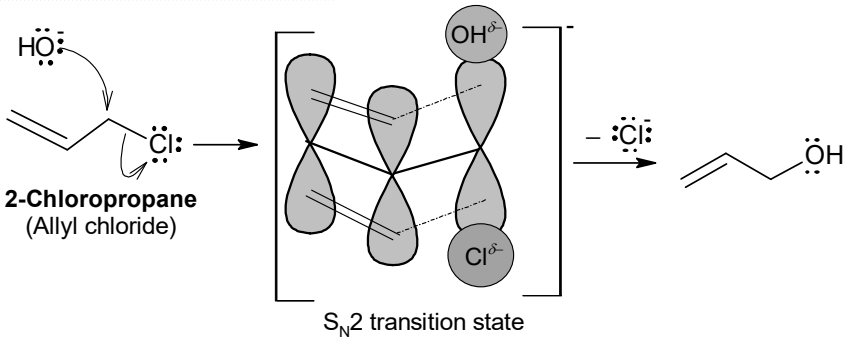
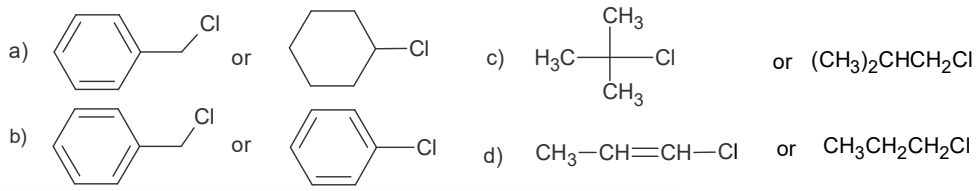


Fig. 13.4: Stabilisation of S_N2 transition state through overlap of the *p*-orbitlas of π bond and *p*-orbital that formed on rehybridisation of carbon centre.

SAQ 6

Which member of each of the following pairs would undergo the faster S_N2 reaction? Explain your answer.



Hydrolysis of Alkyl Halides

Hydrolysis of alkyl halides can be achieved by simply water or aqueous solution of NaOH and KOH. Methanol or ethanol is also added to the aqueous solution to dissolve alkyl halide.

The reaction between a primary alkyl halide and water is very slow even if they are heated. In this reaction, halogen atom is replaced by –OH through S_N2 mechanism. For example, consider the reaction of typical primary alkyl halide,1-bromoethane:

$$CH_3CH_2Br + H_2O \longrightarrow CH_3CH_2OH + HBr$$

With water, nucleophilic substitution is very slow because water is not a very good nucleophile. But if we add hydroxide ion, the hydrolysis will be faster than just water because the hydroxide ion is a more powerful nucleophile. Although water and hydroxide ion are electron pair donors, the hydroxide ion carries a full negative charge which enhances the nucleophilicity of hydroxide ion compared to the electrically neutral water molecule.

Now consider the reaction of a tertiary alkyl halide with water, when it is heated under reflux with water, the halogen is replaced by —OH to give an alcohol. This reaction happens much faster than the corresponding one involving a primary alkyl halide and it follows S_N1 mechanism. For example:

$$(CH_3)_3Br + H_2O \longrightarrow (CH_3)_3COH + HBr$$

The rate of the overall reaction is governed entirely by how fast the alkyl halide isionised. In this case addition of hydroxide ion doesn't affect the

reaction rate. The water/OH^- is not involved in the slow step of the reaction. Thus, this reaction is generally carried out in water in place of aqueous solution of NaOH or KOH. Secondary alkyl halides follow both S_N2 and S_N1 mechanism not as fast as we observed in case of tertiary alkyl halide. This relative reactivity of alkyl halide may be used in identification of primary, secondary and tertiary alkyl halides using alcoholic silver nitrate solution. The tertiary halide produces a precipitate of silver halide almost instantly and the secondary halide gives a slight precipitate after a few seconds. The precipitate thickens up with time. The primary halide may take considerably longer to produce a precipitate.However, aryl halides and alkenyl halides will not react with alcoholic silver nitrate.

Reaction with Cyanide Ion:

Alkyl halide on treatment with a solution of sodium or potassium cyanide in ethanol, gives a nitrile. The cyanide ion is a good nucleophile as there is a formal negative charge and a lone pair on the carbon atom.

For example, using 1-bromobutane as a typical primary alkyl halide:

$$CH_3CH_2CH_2CH_2Br + :CN^- \longrightarrow CH_3CH_2CH_2CH_2CN + Br^-$$

In this reaction, bromine is simply replaced by a —CN groupby S_N2 mechanism and gives pentanenitrile (Butyl cyanide). A small amount of pentaneisonitrile is also formed in the above reaction. Secondary and tertiary alkyl halides also behave similarly, although the mechanism will vary depending on which type of alkyl halide you are using.

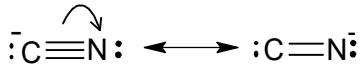
This reaction is very useful as it affords a method of adding one carbon atom to a chain. The resultant nitrile can be either hydrolysed by heating with dilute acid to a carboxylic acid:

$$CH_3CH_2CH_2CH_2CN + 2H_2O + H^+ \longrightarrow CH_3CH_2CH_2CH_2COOH + NH_4^+$$

or it can be transformed into an amine by reaction with hydrogen at 423 K in the presence of a nickel catalyst:

$$CH_3CH_2CH_2CH_2CN + 2H_2 \longrightarrow CH_3CH_2CH_2CH_2CH_2NH_2$$

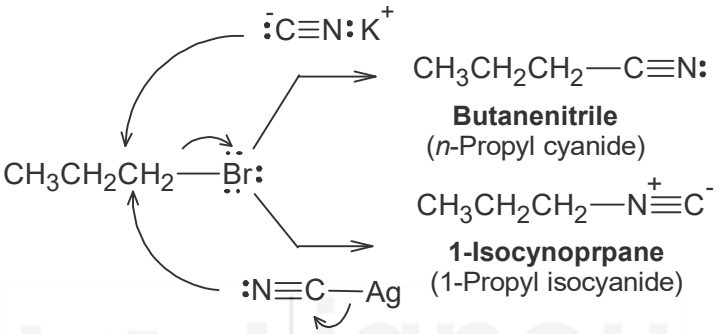
The reaction of AgCN with alkyl halides produces mainly isonitrile, RNC, in contrast to similar reactions discussed above with alkali metal cyanide (NaCN and KCN), which yield mostly nitriles. This is because of the presence of two nucleophilic centres in cyanide ion. In fact cyanide ion has two resonating structures as shown below:



I II

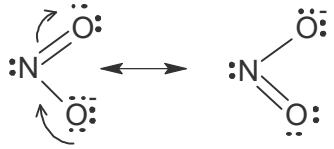
Therefore, it may react either by carbon or nitrogen centre. Such nucleophilic species which have more than one site for reaction are called ambident nucleophiles. Alkali metal cyanides such as NaCN and KCN,are ionic compounds and dissociate as cyanide ion and metal ion. In cyanide ion, carbon centre is a better nucleophile than nitrogen centre because it has full

negative charge besides having a lone pair; therefore, cyanide normally reacts with alkyl halide through its carbon centre and giving nitrile as major product. On the other hand, silver cyanide is predominantly covalent, therefore, silver remain bonded to carbon of cyanide group and leaving the nitrogen end free to be nucleophilic (whereas potassium or sodium ions is not so attached to cyanide ion during reaction). Thus, only nitrogen centre is available for the attack on electrophilic centre of alkyl halide. As a result, alkylisonitriles are formed as main products. Silver cyanide also promotes an S_N1 reaction, as the silver interact with the halide ion, forming carbocation or enhancing carbocation character of transition state. Now comparatively weak nitrogen nucleophilic centre of cyanide ion can attack on such activated carbon centre and forming alkylisonitrile as major product. Products formed during the reaction of 1-bromopropane with potassium cyanide and silver cyanide are shown below.



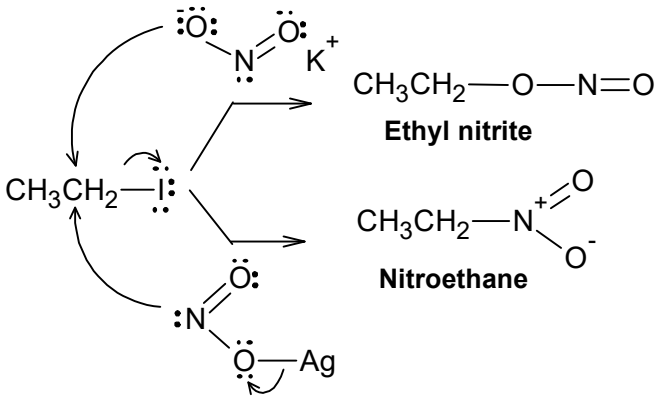
Reaction with Nitrite Ions

Similar to cyanide ion, nitrite ion is also an ambident nucleophile with two different nucleophhilic centres, i.e. one through oxygen results formation of alkyl nitrite and other through nitrogen gives nitroalkanes.



Resonance stabilised nitate ion

Alkyl halides react with alkali metal nitrites i.e. $NaNO_2$ or KNO_2 to give corresponding alkyl nitrates as the major product along with nitroalkanes as minor product. However, when alkyl halides are treated with silver nitrite ($AgNO_2$), nitroalkanes are formed as major product.



Alkali metal nitrites ($NaNO_2$ and KNO_2) are predominately ionic compounds; therefore, nitrite ion attacks mainly trough better nucleophilic site i.e. negative charged oxygen to electrophilic centre of alkyl halide to form alkyl nitrite. On the other hand, silver nitrate is covalent in nature and remains bonded to oxygen atom of nitrite group and leaving the nitrogen end free to be nucleophilic. This nucleophilic nitrogen through its lone pair of electrons attacks and as a result, nitro compounds are formed as major products.

Reaction with Metals

Alkyl halides react with certain metals to give compounds containing carbon-metal bonds. Such compounds are known as organo-metallic compounds.

For example, the reaction of chloroethane with a sodium lead alloy under pressure gives tetraethyllead.

$$2\,C_2H_5{-}Cl + 4\,Na/Pb \longrightarrow (C_2H_5)_4Pb + 4\,NaCl$$

Chloroethane **Tetraethyllead**

Tetramethyl and tetraethyl-lead are used as anti-knock additives to petrol.

An important class of organo-metallic compounds discovered by Victor Grignard in 1900 is alkyl magnesium halides, RMgX, referred as Grignard Reagents. These reagents are obtained by the reaction of alkyl halide with magnesium metal in dry ether.

$$R{-}X \xrightarrow{Mg \text{ in ether}} RMgX$$

In the Grignard reagent, the carbon-magnesium bond is covalent but highly polar, with carbon pulling electrons from electropositive magnesium and making the carbon atom both nucleophilic and strongly basic; the magnesium halogen bond is essentially ionic.

$$R{-}\overset{\delta^-}{C}H_2{-}Mg^+X^-$$

Carbon is a nucleophilic centre

Grignard reagents, therefore, take part in nucleophilic addition reaction. Grignard reagents are used to prepare a large variety of organic compounds. Some of the important reactions are:

i) **Preparation of alkanes:** Alkanes are prepared by the reaction of Grignard reagents with water, alcohols, ammonia, amines etc.:

$$RMgX + H_2O \rightarrow RH + Mg(0H)X$$

Water Alkane

$$RMgX + R'OH \rightarrow RH + Mg(OR')X$$

Alcohol

$$RMgX + NH_3 \rightarrow RH + Mg(NH_2)X$$

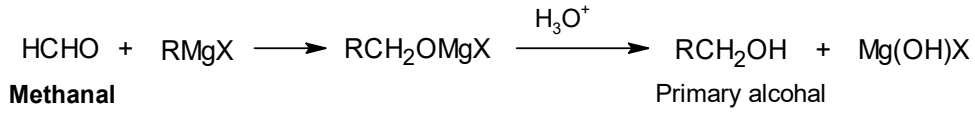
Ammonia

$$RMgX + R'NH_2 \rightarrow RH + Mg(NHR')X$$

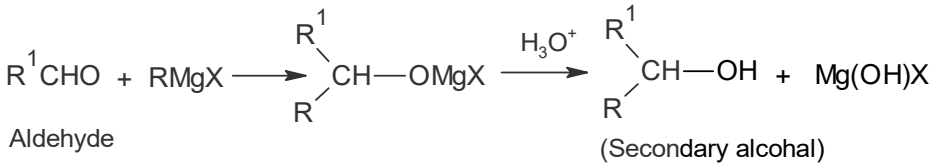
Amlne

In these reactions Grignard reagents act as very strong bases and react with any source of proton (acid) to give hydrocarbons. It is therefore, necessary to avoid even traces of moisture while using a Grignard reagent.

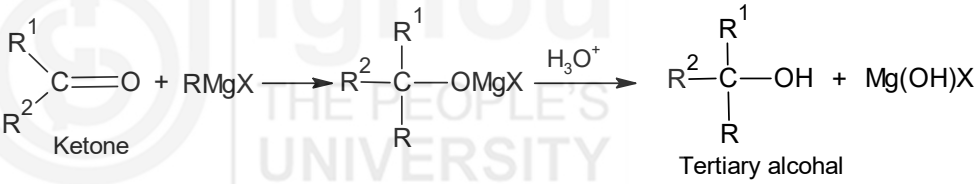
ii) **Preparation of alcohols:** Primary alcohols are obtained by the reaction of methanal and Grignard reagent followed by treatment with dilute acid:



Secondary alcohols are obtained when a Grignard reagent is treated with anyaldehyde (other than methanal) followed by decomposition of the addition product with a dilute acid:

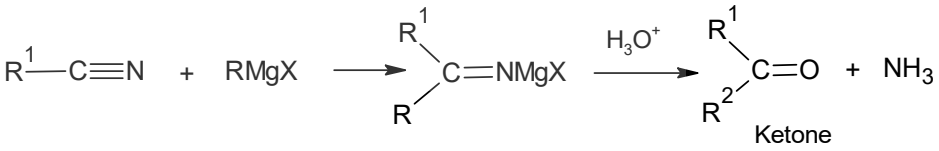


Tertiary alcohols are obtained on treatment of a ketone with Grignard reagent and subsequent addition of dilute acid:

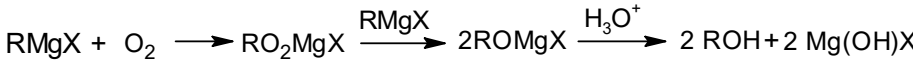


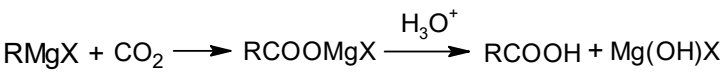
Alcohols are also obtained when epoxides are reacted with Grignard reagent and the addition product is hydrolysed with dilute acid:

iii) **Preparation of Ketones:** Ketone can be prepared by the reaction of an alkyl nitrile with a Grignard reagent:



Grignard reagents also react readily with oxygen and carbon dioxide as shown below. These side reactions can be prevented by forming the Grignard reagent under an inert atmosphere such a nitrogen.





Another side reaction that occurs during the formation of Grignard reagents is the coupling reaction between two alkyl (or aryl) halides as shown below. This side reaction can be minimized if the concentration of the halide is kept low by the slow addition of an ether solution of the halide to a mixture of magnesium and ether.

$$RX + RMgX \xrightarrow{\text{Ether}} RR + MgX_2$$

This reaction is similar to Wurtz reaction which you have studied earlier.

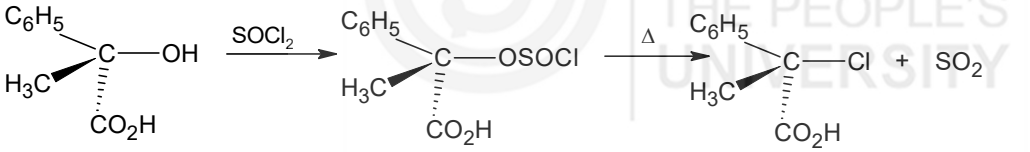
Using the reactions discussed above, attempt the following SAQ.

SAQ 7

How would you prepare primary, secondary and tertiary alcohols? Give one reaction for each case.

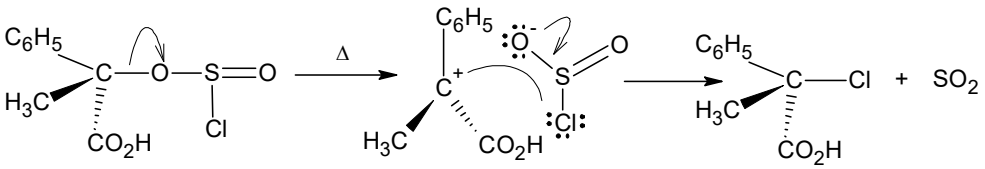
SNi Reaction

So far we have discussed substitution reactions which involve two reactants, a substrate (alkyl halide) and a nucleophile. In some substitution reactions, the nucleophile is a part of the substrate. Such intramolecular substitutions are more rapid than the corresponding intermolecular reactions. Consider following reaction:



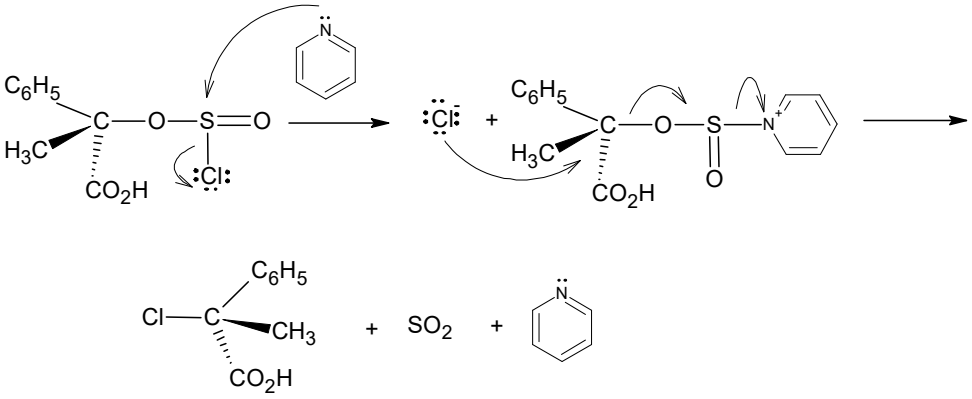
This reaction is said to proceed by S_Ni mechanism meaning substitution nucleophilicinternal (intramolecular), since both the nucleophile and the leaving group are part of a single molecule. Stereochemistry of these reactions shows retention of configuration at the chiral carbonatom i.e. nucleophile attacks from the same face as the leaving group departure.

The first step is like that an S_N1 reaction, i.e., formation of ion pair. In the second step, a part of the leaving group attacks only from the front side leading to retention of configuration.



Chlorine attacks carbocation on same face of tight ion pair

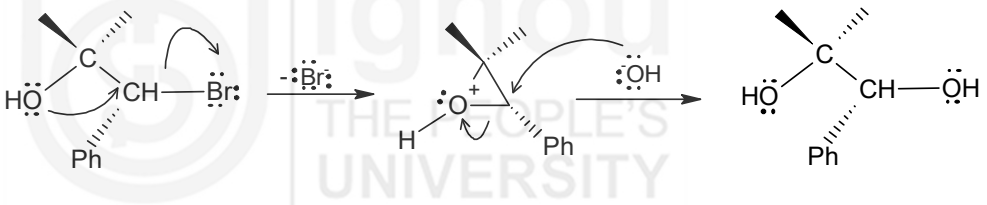
If, however, an external chloride ion is available in the presence of an amine like pyridine, a normal S_N2 reaction occurs in the above case with inversion of configuration.



Result is inversion

The S_Ni reaction mechanisms did not meet with wide acceptance, even though in chemical literature this In gold system is still utilised to describe similar types of substitution reactions.

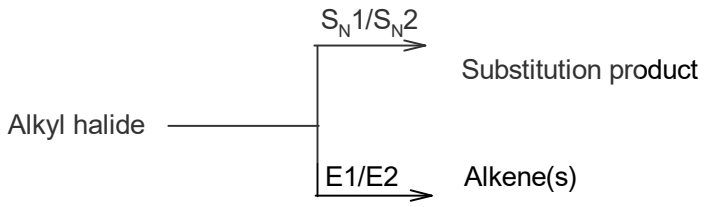
Finally, neighbouring group participation can occur to produce the same result as S_Ni - i.e. overall retention of configuration in product. For example, if the molecule in question has a nucleophilic substituent that can reach the electrophilic site, then that substituent may participate in the reaction as well as the incoming nucleophile. If the electrophilic site is chiral, there will be overall retention rather than inversion, as shown in the following example;



It is worth noting that both steps of this reaction involve the S_N2 mechanism, with inversion, so the overall result (of double inversion) is retention.

Elimination Reactions

A side reaction that occurs during substitution reactions of alkyl halides is the elimination of HX (dehydrohalogenation) to produce an alkene.

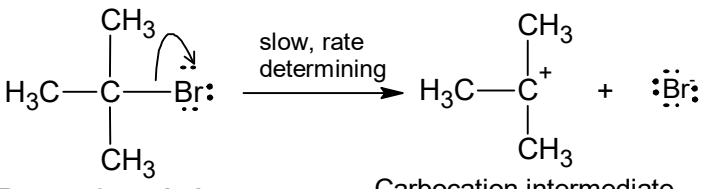


Under appropriate conditions such as the use of a strong base (OH^- or OR^-), and high temperature, elimination can be the principle reaction and thus become a method for the preparing alkenes. We have already introduced such reaction in Unit 16 of first semester course.

Like the nucleophilic substitution reactions, elimination reactions of alkyl halides can proceed by either a first or a second order mechanism. The first order elimination reaction is symbolised as E1 and the second order elimination reaction as E2.

E1 reaction: In the absence of a strong base tertiary alkyl halides, and to some extent secondary alkyl halides, dehydrohalogenate via the E1 mechanism to give alkenes. The mechanism has two steps.

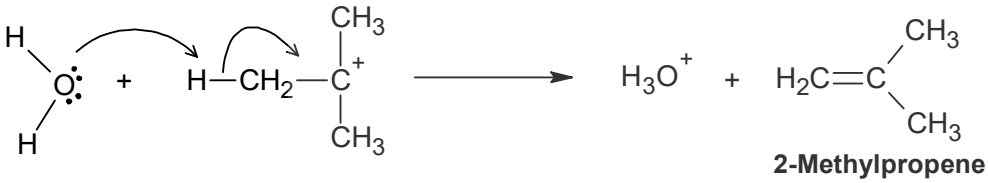
Step 1 (slow): Ionisation of the C–X bond gives stable carbocation:



2-Bromo-2-methylpropane
(*tert*-Butyl bromide)

Carbocation intermediate

Step 2: Proton transfer from carbocation intermediate to form alkene:



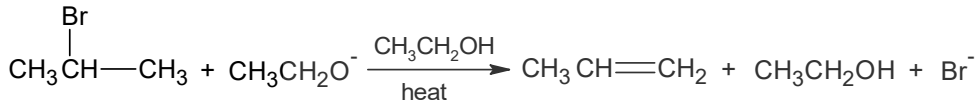
2-Methylpropene

The first step, as in S_N1 reactions is ionisation of the alkyl halide. Since, this is the slow i.e., rate determining step the E1 reaction follows first order kinetics.

Note that the base here attacks the hydrogen atom and not the carbon carrying the positive charge.

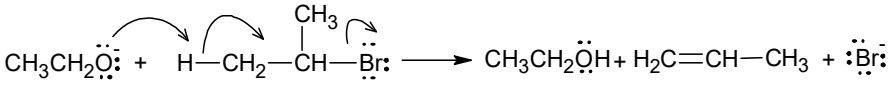
E1 reactions of alkyl halides occur under the same conditions as S_N1 reaction (polar solvent, very weak base etc.) Therefore the E1 reaction is a strong competitor of the S_N1 reaction. The order of reactivity of different halide types is the same in both reactions, that is *tert* > *sec* > *p*. The E1 reaction is favoured by the higher temperature and is most common in tertiary halides.

E2 reaction: The most useful elimination reaction of alkyl halides is the E2 reaction (bimolecular elimination). The E2 reactions of alkyl halides are favoured by the use of strong bases, such as OH^- or OR^- and high temperature. Typically the E2 reaction is carried out by heating the alkyl halide with KOH or $NaOCH_2CH_3$ in ethanol.



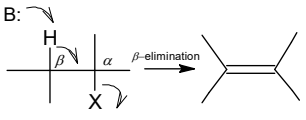
2-Bromopropane **Ethoxide ion** **Propene**

A mechanism consistent with the rate-law is given below, in which the proton and the halide ion are removed simultaneously to give the alkene i.e. bond breaking and bond forming are concerted.

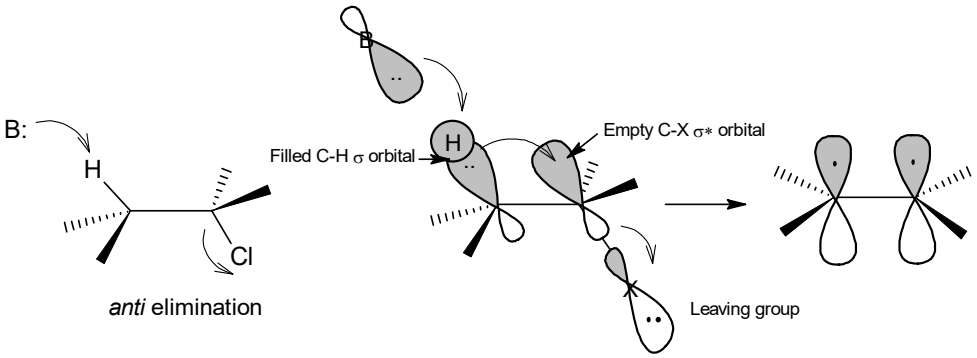


Stereochemical studies reveal that E2 elimination reactions are stereoselective *anti*-eliminations. The anti-elimination involves all backside electronic displacements.

E2 elimination reaction is an example of *β*-elimination. In a *β*-elimination reaction two groups are eliminated from adjacent atoms. It is by far the most common type of elimination reaction in organic chemistry.



Backside attack of the base on the C−X bond



Similar to S_N2 reactions, there is an orbital-based reason for the anti-elimination. This can be explained using molecular orbital approach. You can see in above diagram that filled C−H *σ* bonding molecular orbital aligned with the empty C−X *σ** antibonding molecular orbital. As the strong base removes the proton, the two electrons moves from C−H *σ* bonding orbital to empty C−X σ* antibonding orbital and thereby breaking the C−X bond. This anti and coplanar arrangement of the molecular orbitals leads to proper phasing to form new π bond.

Substitution versus Elimination

We have said earlier that substitution and elimination are competitive reactions; one reaction occurs at the expense of the other. Now, we consider the important factors which determine the direction of the reaction.

i) The structure of the alkyl halide,

ii) The nature of the base, and

iii) Temperature.

We have summarized the effect of these variables in Table 13.8.

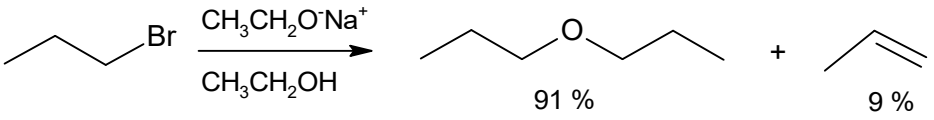
Table 13.8: Substitution versus Elimination

Alkyl Halide	Weak base	Moderate base	Strong base
Primary Alkyl halide	S_N2	S_N2	S_N2 with good nucleophile and E2 with poor nucleophile and high temperature
Secondary Alkyl halide	S_N1 or S_N2; Some E1 at high temperature	S_N2; E2 at high temperature	E2
Tertiary Alkyl halide	S_N1 and E1; E1 predominates at higher temperature	E2	E2

In general, branching in alkyl halides and higher temperature increases the ratio of elimination to substitution.

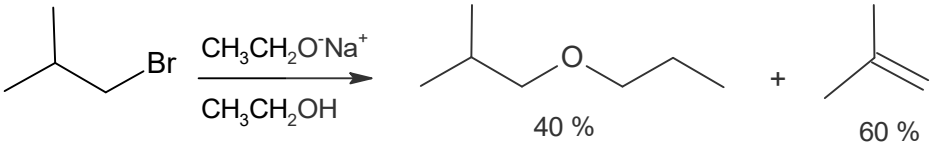
To further understand effect of above factors, we will now consider some specific examples and analyse the factors that determine the direction of the reaction.

Example 1



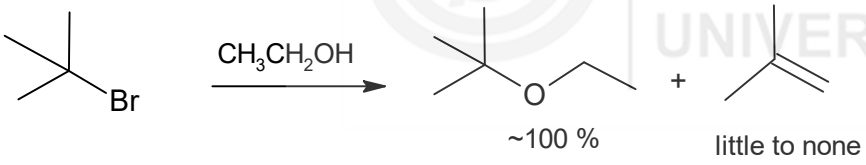
In above example alkyl halide is primary and therefore the major reaction is S_N1 and E1 is a minor reaction. Further, ethoxide ion is strong base as well as a good nucleophile, therefore, S_N2 reaction dominated over E2 reaction.

Example 2



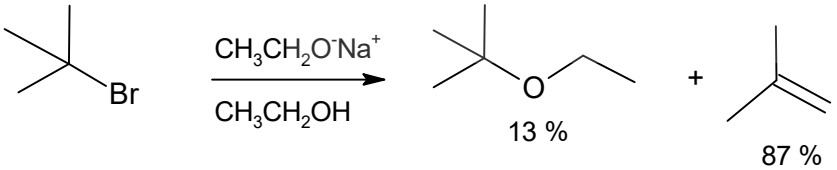
Because of branching in primary alkyl halide (steric factor) in this case this will give nearly equal amount of S_N2 and E2 reactions. Similar reaction with secondary alkyl halides will be dominated by E2 reaction.

Example 3

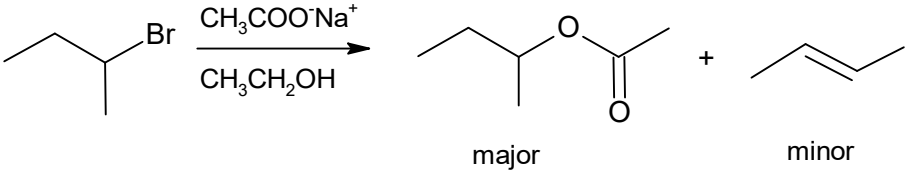


Here, ethanol is a weak base i.e. weak nucleophile and alkyl halide is tertiary, therefore S_N2 and E2 reaction can easily be ruled out. It is expected that this reaction will follow SN1 and E1. Generally, E1 only is a minor reaction.

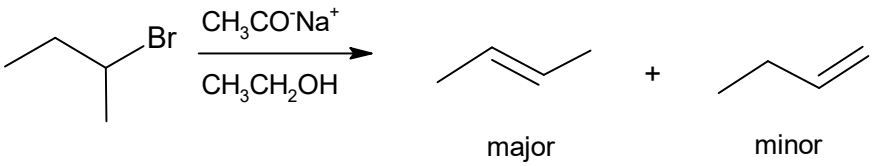
The reaction of the same alkyl halide with strong base such as sodium ethoxide in ethanol, follows E2 reaction predominantly.



Example 4



This reaction alkyl halide is secondary and acetate ion is weak base. Therefore, there will be little or no E2 reaction. This reaction predominantly follows S_N2 reaction. If same alkyl halide is treated with strong base such as $NaOC_2H_5$ in ethanol, E2 would have been the dominated reaction.



In this above reaction, formation of more substituted alkene is dominated over less substituted alkene. More substituted alkene is thermodynamically more stable than the less substituted alkene. Hence, products of such reaction are governed by the relative stability of products. In *β*-elimination reactions, relative stability of products provides a rationale for the Saytzeff rule of regiochemistry. Now, let us discuss this rule.

Saytzeff rule: In the alkyl halides, where the halogen is not attached to the terminal carbon atom, elimination is possible in two directions, giving two isomeric alkenes. An illustrative example is the dehydrobromination of 2-bromobutane to give 1- and 2-butenes:

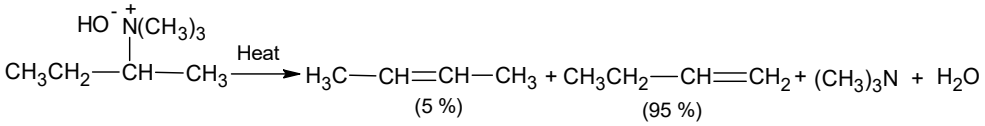
2-Bromobutane **2-Butene** (Preferred product) **1-Butene**

In the above reaction, the major product is 2-butene. This follows the rule formulated in 1875 by Alexander Saytzeff. Saytzeff rule states that in a dehydrohalogenation reaction of alkyl halides, **the major product will be the one that has the more alkyl groups attached to the resultant carbon-carbon double bond.** The rule parallels the order of thermodynamic stability of the alkenes; that is, the alkene with more alkyl groups attached to the carbon-carbon double bond is more stable.The order of stability of alkenes may be represented as:

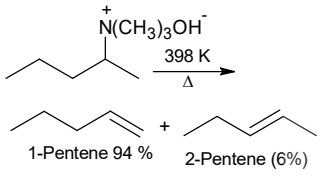
$R_2C{=}CR_2 > R_2C{=}CRH > RHC{=}CHR$ and $R_2C{=}CH_2 > RCH{=}CH_2$

Because of the relative stability of the resultant alkenes, tertiary halides undergo dehydrohalogenation more readily than secondary halides, which dehydrohalogenate more readily than primary halides (as we have already noticed earlier).

Exceptions to the Saytzeff rule are exemplified by the Hofmann rule. This rule predicts that *β*-elimination will occur preferentially to gives the less substituted alkene as major product. For example thermal decomposition of *sec*-butyltrimethylammonium hydroxide gives 1-butene as the major product.



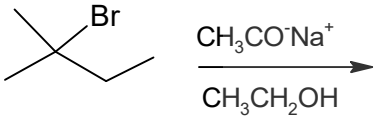
Elimination reaction in quaternary ammonium hydroxides ($R_4N^+OH^-$) does 'not follow Saytzeff rule, but they undergo elimination reactions and yield the Hofmann product, the alkene with fewer alkyl groups on the *π*-bonded carbons. Such reactions are known as Hofmann eliminations and follow E2 mechanism. The formation of the less substituted less stable alkene can be attributed to steric hindrance in the transition state stability (relative transition state energies) due to the group, e.g..butyl in the example given below:

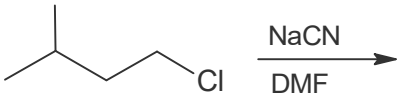


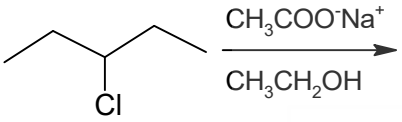
If there are more than one *β*-hydrogen is anti to leaving group, then there will be competition between Hofmann and Saytzeff elimination. Eliminations involving halide ions or negative charged leaving groups generally follow Saytzeff rule, unless a bulky base is used. On the other, if leaving group is neutral in nature such as $N(CH_3)_3$ and $S(CH_3)_2$, the eliminations will follow Hofmann rule. Bulkier bases such as $(CH_3)_3COK$ also predominantly give Hofmann product. The regioselectivity of *β*-elimination can be explained on the bases of relative stability of transition state during elimination reaction.

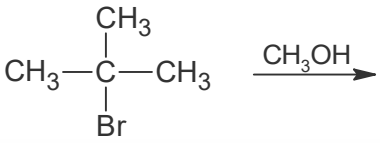
SAQ 8

Predict whether each reaction proceeds predominantly by S_N1 or S_N2 or E1 or E2.

a) 

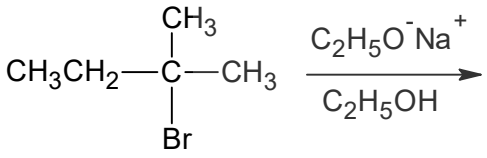
b) 

c) 

d) 

SAQ 9

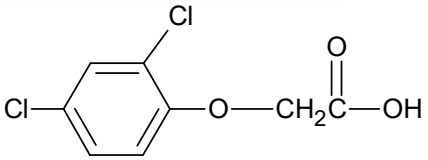
Write the equation for the formation of alkenes from the following starting material. If you expect more than one product, indicate which alkene is the major product.



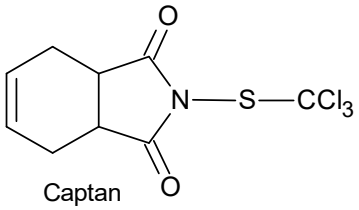
13.4.5 Uses of Alkyl Halides

Alkyl halides find a variety of uses and applications in our everyday lives. They are used in labs as synthetic intermediate compounds and as solvents. Dichloromethane (CH_2Cl_2, methylene dichloride), trichloromethane ($CHCl_3$, chloroform), tetrachloromethane CCl_4, carbon tetrachloride) and trichloroethylene ($Cl_2C=CHCl$), for example, are used as solvents.

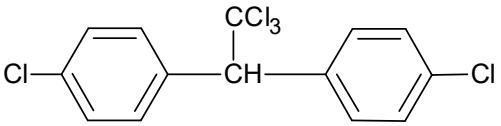
In agriculture, alkyl halide such as2,4-D applied as herbicides captan as fungicides. The insecticide DDT (1,1,1-trichloro-2,2-bis(*p*-chlorophenyl)ethane) is effectively used to control many diseases such as malaria, typhus, and cholera. Most countries have banned the use of DDT. Since DDT accumulates in fatty tissue of warm-blooded animals (and humans), it was suspected to be carcinogenic. Latter, this assumption has been proven not to be correct.



2,4-D



Captan



DDT

Until the mid-1980s, chlorofluorocarbons (CFCs) were produced in large quantities. They are derivatives of methane and ethane. Freons such as trichlorofluoromethane (freon-11), tetrafluoromethane (freon-14) and trichlorotrifluoroethane (freon-113), for example, are relatively simple CFCs in which all hydrogen atoms have been substituted by chlorine or fluorine atoms. They are prepared by the action of hydrogen fluoride on tetrachloromethane (carbon tetrachloride), trichloromethane and hexachloroethane. CFCs are produced at a reasonable price and are stable, non-toxic, non-inflammable, and non-corrosive. Therefore, CFCs were considered perfect materials for usage in many practical applications, including propellants, coolants in refrigerators and fire-extinguishing agents. Unfortunately, due to their high chemical stability, CFCs have been identified as a severe environmental liability. They are a main cause of ozonolysis in the stratosphere and are largely responsible for the ozone hole. As a result, the production of CFCs is prohibited worldwide. However, due to their high stability, the CFC concentration in the stratosphere will not considerably decrease to a safe level until the year 2050. Now, CFCs are replaced by third generation products such as hydrofluorocarbons (HFCs).They do not harm the ozone layer as much but these products more expensive to produce than CFCs.

Tetrafluoroethene ($CF_2=CF_2$) on polymerisation gives aplastic **Teflon.** It is unaffected by chemical reagents, even by boiling aqua regia. It is widely used as a liner in frying pans and on other utensils and tools to provide nonsticking surfaces. Polychlorofluoroethenes are used as oils and greases. Perfluoroheptane is used in the separation of uranium isotopes. Poly (chloroethene) .or polyvinyl chloride (PVC) is a plastic material of commercial importance.

At present, more than 15,000 halogenated organic compounds are produced for industrial purposes. They are used as feedstock for the production of PVC, industrial lubricants, pesticides, insecticides, herbicides, solvents and many others. However, the fact that many of these compounds are either not at all or only barely biodegradable has serious implications on health and environment. Simple compound, carbon tetrachloride used as a fabric cleaner is known to cause damage to liver. Similarly, chloroform a popular anesthetic has been proven to be cancerous. Therefore, use and circulation of alkyl halides has been restricted to some extent.

13.5 LAB DETECTION

The presence of halogen in an organic compound is readily detected by the **Beilstein test.** In this test a small amount of the compound is placed on a small loop of copper wire, and the loop heated in a flame. A green flame is evidence of the presence of halogen. To ascertain which halogen is present, the covalently bonded halogen has to be converted to the halide ion which can then be identified by the usual methods of inorganic qualitative analysis. This is done by two methods; through sodium fusion (treatment with hot molten sodium metal):

$$Na + \underset{\text{Organic compound}}{RX} \xrightarrow{\text{Heat}} Na^{+}X^{-}$$

or through Schoniger oxidation by oxygen gas under alkaline condition

$$\underset{\text{Organic compound}}{RX} + O_2 \xrightarrow{NaOH} Na^{+}X^{-} + H_2O$$

In alkyl halides, benzyl halides and allyl halides the presence of halogen can be detected by warming the organic compound with alcoholic silver nitrate. The silver halide formed can be analysed further.

$$\underset{\text{Organic compound}}{RX} + AgNO_3 \xrightarrow{NaOH} AgX(s)\downarrow + RONO_2$$

However, aryl halides and alkenyl halides will not react with alcoholic silver nitrate.

The reaction helps in distinguishing alkyl halides from aryl and alkenyl halides.

13.6 SUMMARY

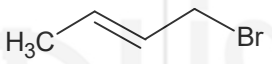
In this unit, we have described the chemistry of alkyl halides. We are summarising below what we have studied:

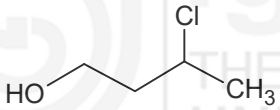
- Substitution of one or more hydrogen atoms in alkanes by a halogen atom(s) gives rise to alkyl halides. Monohalogen derivatives of alkyl halide can be further classified as primary, secondary and tertiary halides depending on the alkyl group to which halogen is attached.
- Alkyl halides can be prepared from alcohols, from alkanes, from Grignard reagents and through halogenation of hydrocarbons in the presence of light or heat and catalysts.
- The halogen in alkyl halides can be replaced by various nucleophiles. These reactions occur by two different pathways, S_N1 and S_N2. Benzyl and allyl halides are more reactive than alkyl halides. Aryl and vinyl halides are least reactive and theydo not follow S_N2 and S_N1 paths. The reactivity order of halides is allyl > benzyl > alkyl > aryl or vinyl.

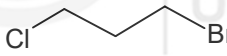
- Alkyl halides undergo elimination reaction (dehydrohalogenation) to give alkenes. These reactions occur by the E1 or E2 pathway. If the halides are such that the lossof a hydrogen on adjacent carbon *(β*-hydrogen) can occur from either side, isomeric alkenes are formed. Usually, the most stable i.e. more highly substituted alkene is formed as the major product (Saytzeff rule).
- Alkyl halides react with magnesium to form alkyl magnesium halides, called the Grignard reagents. They are very reactive compounds and take part in many reactions to give alkanes, alcohols (primary, secondary and tertiary), ketones and carboxylic acids, etc.
- The halogen derivatives are very useful in industry. The chloro compounds are powerful insecticides and moth repellants. The chlorofluoro compounds (Freons) are refrigerants, aerosol and propellants. Polymerisation of vinyl chloride and tetrafluoroethylene gives plastic in the name PVC and teflon, respectively.
- The halogen can be detected as halide ion.

13.7 TERMINAL QUESTIONS

1. Write IUPAC names of the following:

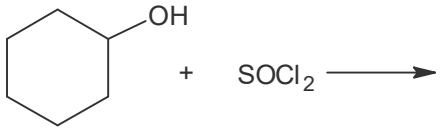
a) 

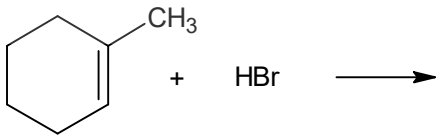
b) 

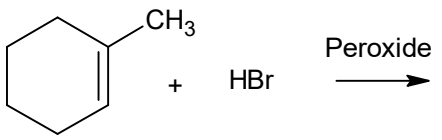
c) 

2. Write the possible isomers for molecular formula C_4H_9Cl. Give IUPAC name for each isomer and also classify them as primary, secondary and tertiary.

3. Write the products of the following reactions:

a) 

b) 

c) 

d) $CH_3COOAg + Br_2 \longrightarrow$

e) $H_2C{=}CHCH_2CH_3 + Br_2 \xrightarrow{Heat}$

f) $CH_3Br + AgF \longrightarrow$

4. Among the following pairs of alkyl halides which would undergo S_N2 reaction faster:

   a) 3-Chloro-1-butene and 4-Chloro-1-butene

   b) 1-Iodopropane and 1-Chloropropane

5. Write the equations for the following reactions:

   a) $CH_3CH_2CH_2CH_2Br + NaOH\ (aq) \rightarrow$

   b) $C_6H_5CH_2Cl + H_2O \rightarrow$

   c) $CH_3CH_2CH_2Br + NaSH \rightarrow$

6. Complete the equations given below:

   a) $CH_3CH_2CH_2Br + CH_3CH_2O^-Na^+ \rightarrow$

   b) $C_6H_5CH_2Cl + AgNO_3 \rightarrow$

   c) Chlorobenzene $+ AgNO_3 \rightarrow$

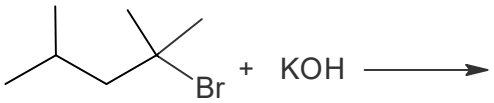
7. a) Reaction of 1-Bromopropanewith sodium cyanide

   b) Reaction of 1-Bromopropane with silver cyanide

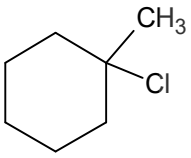
   c) Reaction of 1-Bromopropane with sodium nitite

   d) Reaction of 1-Bromopropane with silver nirite

8. Complete the equation for each of the following reactions and if more than one product is formed, indicate which one is major.

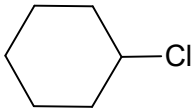
   a) 

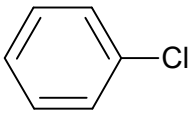
+ KOH $\longrightarrow$

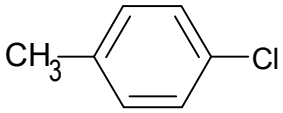
   b) 

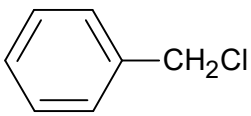
+ $C_2H_5O^-Na^+ \xrightarrow[C_2H_5OH]{\Delta}$

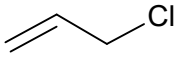
9. Name a simple chemical test or reagent which will readily distinguish between each of the following pair of compounds.

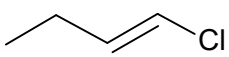
   a) 

and 

   b) 

and 

   c) 

and 

13.8 ANSWERS

Self Assessment Questions

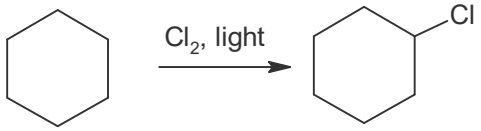
1. a) Secondary alkyl halide, 2-chloro-4-Methylpantane; b) Secondary alkyl halide, 3-Bromopentane; c) Primary alkyl, 1-Chloro-2,2-dimethylpentane; b) tertiary alkyl halide, 2-Chloro-2,4-dimethylpentane.

2. a) $C_6H_5CH_2CH_3 + Br_2 \xrightarrow{h\nu} C_6H_5CHBrCH_3 + HBr$

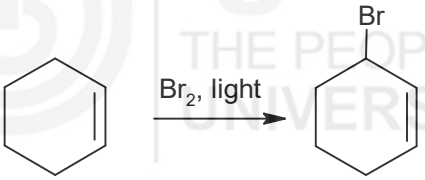
   b) $CH_3CHOHCH_3 \xrightarrow{PBr_3} CH_3CH_2BrCH_3$

   c) $CH_3CH = CH_2 \xrightarrow[\text{Peroxide}]{HBr} CH_3CH_2CH_2Br$

   d) $CH_3CH = CH_2 + Br_2 \xrightarrow[\text{room temp.}]{CH_2Cl_2}$

   a) 

   b) 

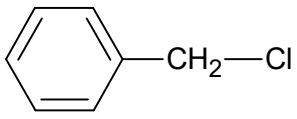
   c) 

4. Increasing order of boiling point of following alkyl halides:

   $CH_3Cl < CH_2Cl_2 < CHCl_3 < CCl_4$

   Since molecular mass and size of compounds is also increasing in the same order.

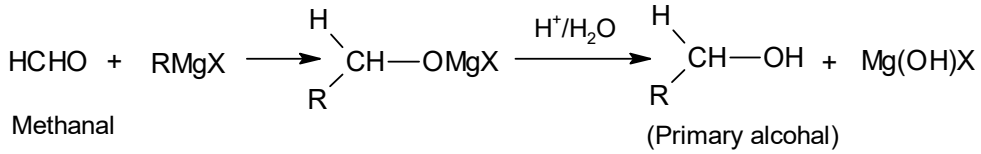
5. The reaction of 2-bromo-2-methylpropane with azide ion follows S_N1 reaction; therefore rate of reaction is proportional to concentration of alkyl halide, so the increase concentration of azide ion does not have much effect on the rate of the reaction.

6. a) and b) 

   In both a) and b) cases (Chloromethyl)benzene (benzyl chloride) undergoes S_N2 reaction at **faster** rate than chlorocyclohexane and chlorobenzene. The reason for greater S_N2 reactivity of (chloromethyl)benzene is the stability of transition state. Further, the low reactivity of chlorobenzene is attributed to the stronger Ar—Cl bond.

c) $(CH_3)_2CHCH_2Cl$ d) CH_2CHCH_2Cl

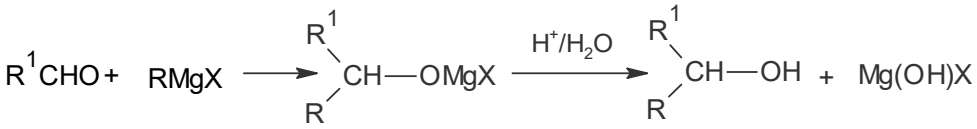
7. Primary alcohols are prepared by the reaction of Grignard reagents with methanal and followed by hydrolysis



Methanal

(Primary alcohal)

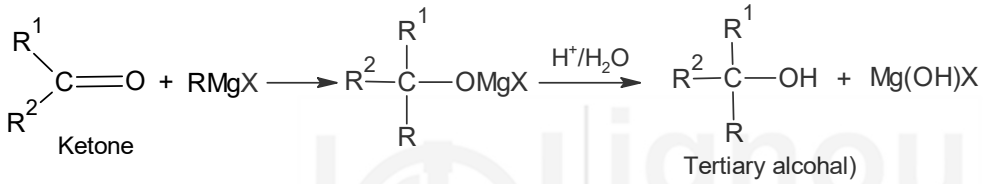
Secondary alcohols are obtained when a Grignard reagent reacts with aldehydes(other than methanal) followed by hydrolysis.



Aldehyde

(Secondary alcohal)

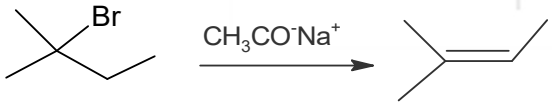
Tertiary alcohols are prepared by the action of a ketone with Grignard reagent and subsequent addition of dilute acid.



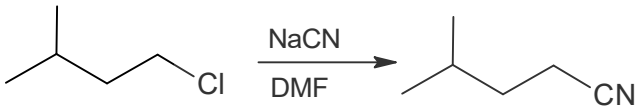
Ketone

Tertiary alcohal)

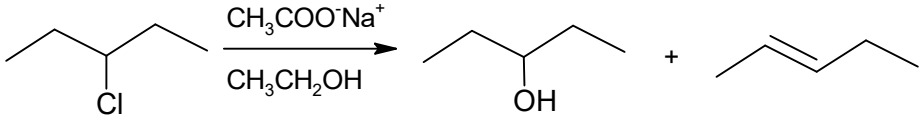
8. a) Major product wills2-methyl-2-butene. This reaction will proceed by E2 elimination as reaction is carried out with tertiary halide in presence of strong base (good nucleophile).



b) Reaction of the primary alkyl halide with a moderate nucleophile such as cyanide ion in presence of polar aprotic solvent will give major substitution product by S_N2 reaction.



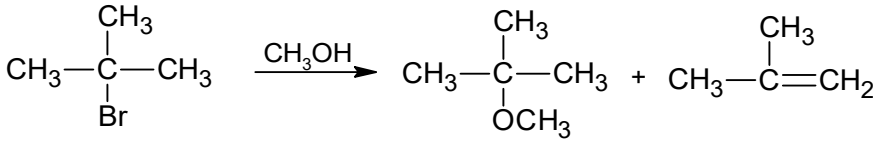
c) Here alkyl halide is secondary and but nucleophile is a weak base. Hence S_N2 will dominate over E2.



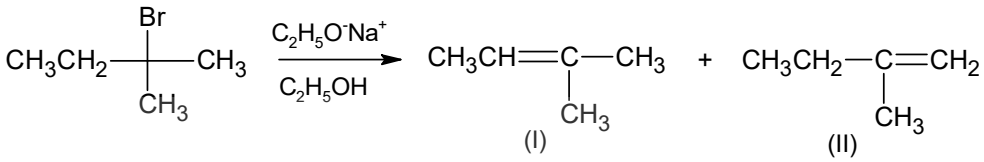
Major

d) Here alkyl halide is tertiary and nucleophile is a weak base so E2 and S_N2 can be ruled out. This reaction will give mixture of substitution

(SN1) and elimination (E1) products. It is difficult to predict the ratio of substitution to elimination products for such reactions.



9. Over all reaction can be written as:



Two products are formed in this case, one (I) is three alkyl substituted alkene and the other (II) is two alkyl substituted, therefore, according to Saytzeff rule (I) alkene will be the major product.

Terminal Questions

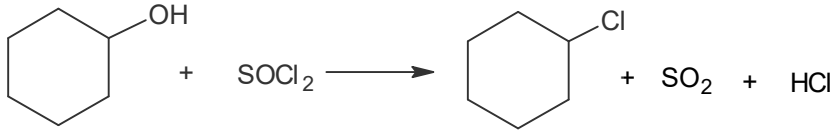
1. a) 4-Bromo-2-butene; b) 3-Chloro-1-butanol; c) 1-bromo-3-chloropropane.

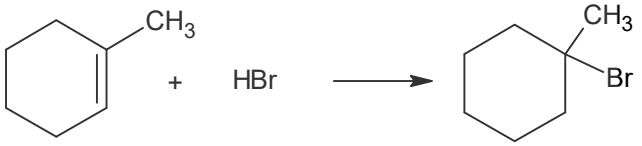
2. a) $CH_3CH_2CH_2CH_2Cl$ Primary 1-Chlorobutane

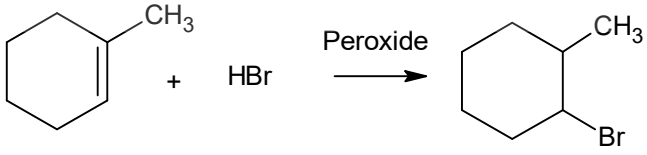
b) $CH_3CH_2CH(Cl)CH_3$ Secondary 2-Chlorobutane

c) $CH_3CH(CH_3)CH_2Cl$ Primary 1-Chloro-2-methylpropane

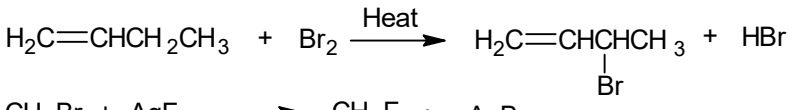
d) $(CH_3)_3CCl$ Tertiary 2-Chloro-2-methylpropane

3. a) 

b) 

c) 

d) $CH_3COOAg + Br_2 \longrightarrow CH_3Br + AgBr + CO_2$

e) 

f) $CH_3Br + AgF \longrightarrow CH_3F + AgBr$

4. a) 3-Chloro-1-butene will undergo S_N2 reaction at faster rate as it is an allyl alkyl halide.

   b) 1-Iodopropane as iodine is better leaving group because of its larger size. It will be released at a faster rate on the attack of a nucleophile.

5. a) $CH_3CH_2CH_2Br + NaOH(aq) \longrightarrow CH3CH_2CH_2OH + NaBr$

   b) $C_6H_5CH_2Cl + H_2O \longrightarrow C_6H_5CH_2OH + HCl$

   c) $CH_3CH_2CH_2Br + NaSH \longrightarrow CH_3CH_2CH_2SH + NaBr$

6. a) $CH_3CH_2CH_2Br + Na^{+-}OCH_2CH_3 \longrightarrow CH_3CH{=}CH_2 + CH_3CH_2OH + NaBr$

   b) $C_6H_5CH_2Cl + AgNO_3 + H_2O \longrightarrow C_6H_5CH_2OH + AgCl$

   c) Chlorobenzene + $AgNO_3$ + $H_2O \longrightarrow$ no reaction.

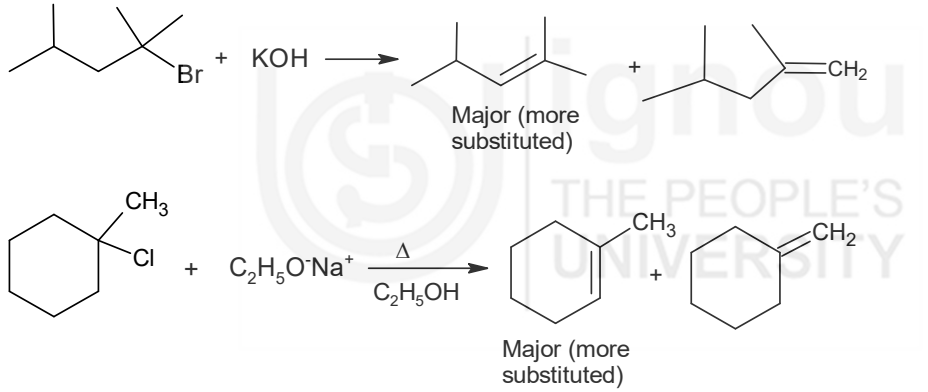
7. a) Butanenitrile

   b) Propylisonitrile

   c) 1-Nitropropane

   d) Propylnitrite

8. a)



9. Following pairs can be distinguished by the action of alcoholic $AgNO_3$ reagent with the halides.

   a) With alcoholic $AgNO_3$ chlrobenzenewill not react

   b) Aryl halide (4-Chlorotoluene) also will not react with alcoholic $AgNO_3$,

   c) $CH_3CH_2CH{=}CHCl$ also will not react with $AgNO_3$.

UNIT 14

ARYL HALIDES

Structure

14.1 INTRODUCTION

In Unit 13, we have pointed out that there is a difference in the nature of C−X bond of aryl halides and aryl halides. Because of this aryl halides differ from the alkyl halides in their preparation and properties. In this Unit, we will study the unique chemistry of aryl halides.

First, we shall take up the structure and reactivity of aryl halides, which is followed by their preparations and properties. At the end of the unit we shall compare the reactivity and relative strength of C−X bond in different type of halogen derivatives.

Expected Learning Outcomes

After studying this unit, you should be able to:

- explain why aryl halides are less reactive than alkyl halides,
- outline the methods of preparation of aryl halides,
- describe the reactions of aryl halides, and
- explain the difference in structure and reactivity of alkyl, alkenyl and aryl halides towards nucleophilic substitution reactions.

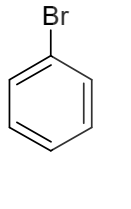
14.2 STRUCTURE AND REACTIVITY

Before going into the details of the preparations and properties of aryl halides let us take a look at the structure and reactivity of these compounds so that we can understand why their reactions are different from alkyl halides.

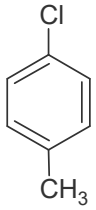
Compounds in which one or more hydrogen atoms of an aromatic ring are replaced by halogen atom(s) are called aryl halides. These compounds are also known as **haloarenes** and have the general formula, Ar–X.

Just to recall, in IUPAC naming of halogens, the prefix – chloro, bromo, iodo etc. is added before the name of arene. The relative position of halogen atoms are indicated by numbers. The prefixes *ortho* (*o*), *meta* (*m*) and *para* (*p*) are also used to indicate the relative positions of substituents.

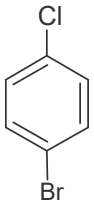
Some representative examples are given below:



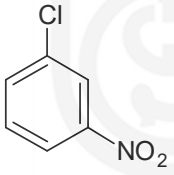
Bromobenzene



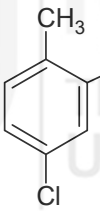
1-Chloro-4-methyl benzene) (*p*-chlorotoluene)



1-Bromo-4-chloro-benzene (*p*-bromo-chlorobenzene)

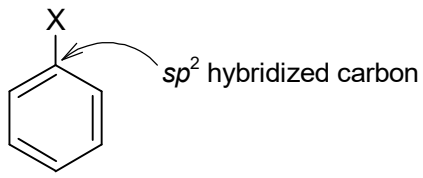


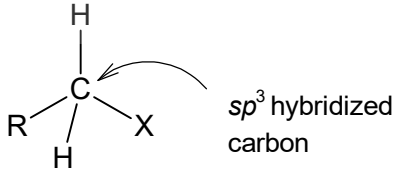
3-Nitrochlorobezene (*m*-nitrochlorobenzene)



2-4-dichloro-methylbenzene (2,4-Dichlortoluene)

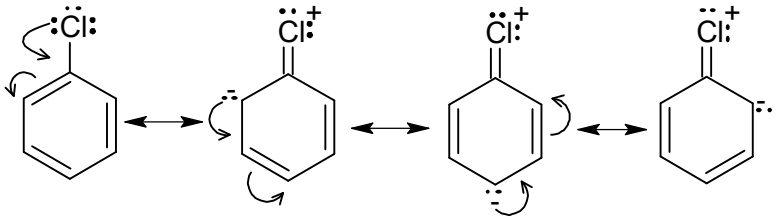
Now, let us focus our attention on the structure and reactivity of aryl halides. It has been discussed earlier that C−X bond in the aryl halide is shorter and stronger because of the difference in hybridisation of carbon atom in C−X bond. In alkyl halides, the carbon atom attached to halogen is sp^3 hybridised while in case of aryl halides, the carbon atom attached to halogen is sp^2-hybridised.



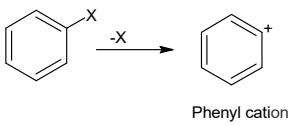


The sp^2 hybridised carbon with a greater *s*-character is more electronegative and can hold the electron pair of C−X bond more tightly than sp^3-hybridised carbon in alkyl halide with less *s*-character. Besides this factor, the unbounded *p*-orbital having electron pairs of the halogen atom can overlap with the π system of the aromatic ring. This will provide partial double bond character in C−X bond (C−Cl bond length in alkyl halide is 177 pm while in aryl halide is 169 pm). The partial

double bond character of C−X bond can be explained by drawing resonating structures for chlorobenzene. The electron pairs on chlorine atom are in conjugation with π-electrons of the ring and the following resonating structures are possible:



Because of these two factors, the C−X bond in aryl halides becomes shorter and stronger in comparison to C−X bond of alkyl halides. Since it is difficult to break a shorter and stronger bond, therefore, aryl halides undergo relatively few reactions involving the carbon-halogen bond.



Phenyl cation

Very difficult to generate phenyl cation

Aryl halides do not undergo substitution by either the S_N1 or S_N2 pathways that are characteristic of nucleophilic substitution reactions in alkyl halides. Elimination reactions also do not occur in aryl halides. Under certain conditions, they do undergo nucleophilic substitution reactions by different mechanism. The reason for the lack of S_N1 reactivity of aryl halide is the difficulty in generation of phenyl cation from a corresponding aryl halide. Phenyl cation, if so formed, as a result of self-ionisation will not be stabilised by resonance. Further, the electron rich aromatic ring reduces δ^+ on carbon atom of C−X bond and also repel approaching electron rich nucleohile for its back side attack (condition needed for S_N2 reaction).

The aromatic ring of aryl halides will react same way as in benzene and will undergo elecrophilic substitution reactions. In these reactions, halogens influence the reactivity and orientation. The halogens are relatively electronegative and have an electron withdrawing inductive effect. Therefore, they deactivate aromatic ring system. On the other hand through its resonance effect halogens activate aromatic ring system. Thus, the inductive and resonance effects of the halogen are counter to each other, but the former is stronger than the latter. Thus the halogens weakly deactivate the ring, and are *ortho-para* directing during electrophilic substitution reactions.

SAQ 1

How do you account for the fact that aryl halides are less reactive towards nucleophilic substitution reactions under ordinary conditions?

SAQ 2

Give explanations for the lack S_N1 and S_N2 reactivity of aryl halides.

14.3 PREPARATION OF ARYL HALIDES

Aryl halide may be prepared by one of the methods given below in Table 14.1

Table 14.1: Preparation of Aryl halide

From Aromatic Hydrocarbons (Direct Halogenations Method)

$$Ar-H + X_2 \xrightarrow[X_2=Cl_2,\ Br_2]{\text{Lewis acid}} Ar-X + HX$$

Lewis acid = $FeCl_3$, $AlCl_3$, $TI(OAc)_3$ etc.

From Aromatic Amines (Diazonium salt method)

$$Ar-NH_2 \xrightarrow[273\ K]{HNO_2/HX} \underset{\text{diazonium salt}}{Ar-N_2^+} \xrightarrow{CuX} Ar-X + N_2$$

CuCl, CuBr

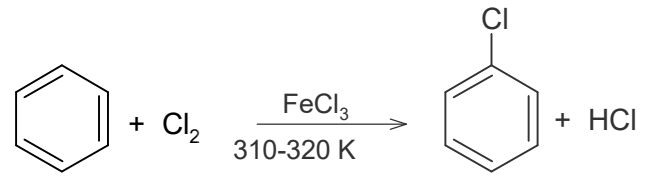
The main drawback of direct halogenations is to get single halogenated product. Generally, with mono-halogenated products, mixture of *ortho* and *para* dihalogenated products are also formed. Thus diazonium salt method is preferred for the preparation of aryl halides.

Let us briefly consider these methods of preparation.

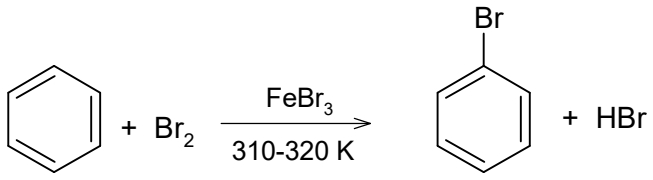
i) **From Aromatic Hydrocarbons:** As discussed in Unit 11, the aromatic halogenation of aromatic hydrocarbon needs the assistance of a Lewis acid as a catalyst. Generally ferric halides or aluminum halides are used as catalysts ($FeCl_3$, $FeBr_3$, $AlCl_3$ etc.).

$$\underset{\text{Aromatic hydrocation}}{Ar-H} + X_2 \xrightarrow[\text{Dark, 310-320 K}]{\text{Lewis acid}} \underset{\text{Aryl halide}}{Ar-X} + HX$$

In actual practice, iron filings in the presence of chlorine or bromine are commonly used. The halogens react with iron filing to form corresponding Lewis acid.

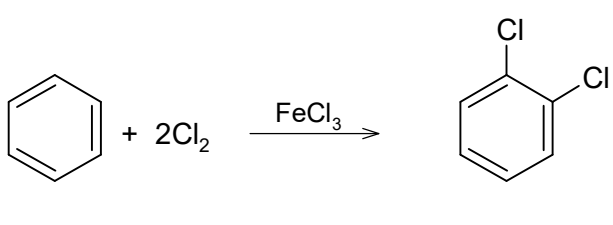


Chlorobenzene



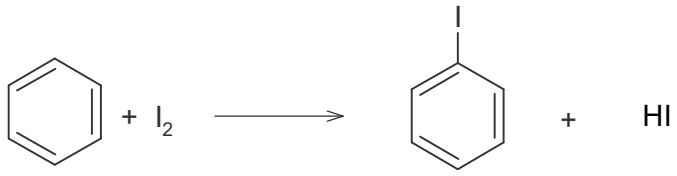
Bromobenzene

If two moles of chlorine (per mole of benzene) are used, a mixture of *ortho*- and *para*-dichlorobenzene is obtained in which the *para* compound predominates for steric as well as electronic reasons.



1,2-Dichlorobenzene (*o*-Dichlorobenzene) **1,4-Dichlorobenzene** (*p*-Dichlorobenzene)

Fluorobenzene and iodobenzene are difficult to prepare by direct fluorination and iodination. The reaction with fluorine is violent and cannot be controlled. Reaction of iodination is reversible. This reaction is carried out in the presence of oxidizing agents such as iodic acid or nitric acid which oxidises HI formed in the reaction to iodine enabling the reaction to proceed in the forward direction.



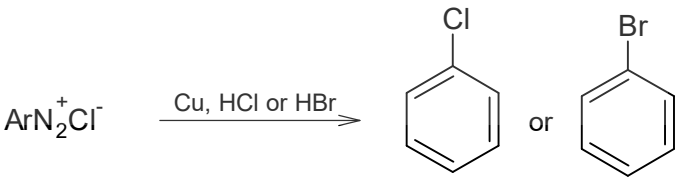
Iodobenzene

$$5HI + \underset{\text{Iodic acid}}{HIO_3} \longrightarrow 3H_2O + 3I_2$$

ii) **From Aromatic Amines:** In this process the amine is first converted to the diazonium salt ($ArN_2^+X^-$), which is then converted to aryl halide using the solution of cuprous halide dissolved in the concentrated halogen acid. This method is known as **Sandmeyer reaction**.

$$\underset{\text{Aromatic amine}}{Ar—NH_2} \xrightarrow[\text{cold}]{NaNO_2–HCl} \underset{\text{Diazonium salt}}{Ar—N_2^+Cl^-} \xrightarrow{CuX/HX} \underset{\text{Aryl halide}}{Ar—X}$$

Copper powder can also be used in place of cuprous halide. This modified reaction is called **Gattermann reaction**.



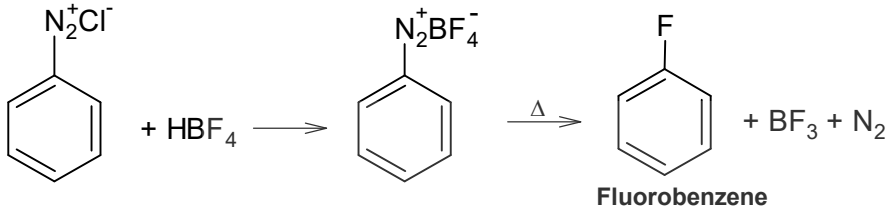
Replacement of the diazonium group by – I does not require the use of a cuprous halide.

$$Ar—N_2^+X^- \xrightarrow{KI} Ar—I + N_2 + KX$$

Chlorobenzene is prepared commercially by the **Rasching process** in which a mixture of benzene vapour, air and hydrogen chloride is passed over copper chloride.

$$C_6H_6 + HCl + 1/2O_2 \xrightarrow{CuCl_2} C_6H_5Cl + H_2O$$

Fluorobenzene cannot be prepared by either Sandmeyer reaction or Gattermann reaction. For preparing fluorobenzene, benzene diazonium chloride is treated with fluoroboric acid. This reaction produces diazomium fluoroborate which, on heating, produce fluorobenzene. This reaction is called **Balz-Schiemann reaction**.



Fluorobenzene

SAQ 3

How the following conversions can be carried out?

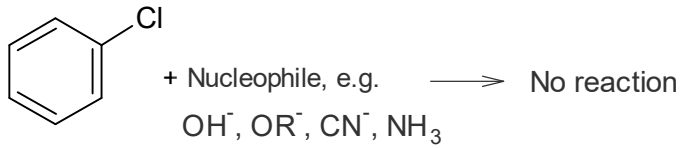
a) Aniline to chlorobenzene

b) Benzene to Iodobenzene

c) Aniline to Fluorobenzene

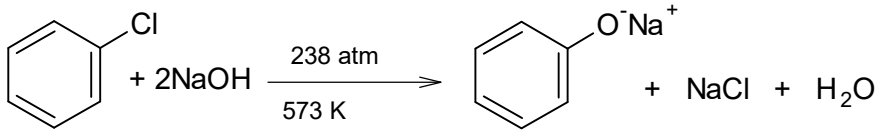
14.4 REACTION OF ARYL HALIDES

As discussed earlier, the aryl halides are relatively unreactive towards nucleophilic substitution reactions; they do not react under ordinary conditions with NaOH, C_2H_5ONa, NaCN, NaSH, H_2O, or NH_3.



Chlorobenzene

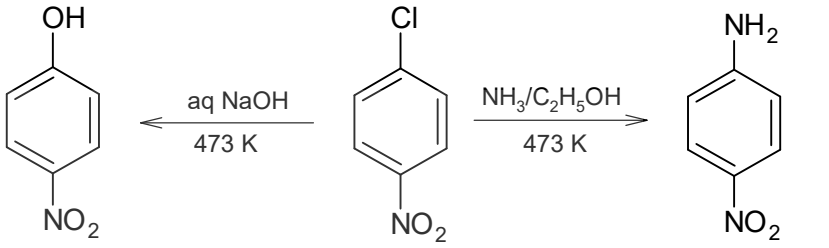
Aryl halides may be forced to react with nucleophiles under drastic conditions such as with very strong base ($NaNH_2$) or with moderate base (NaOH) at high temperature and pressure. For example, chlorobenzene when heated at 573 K under high pressure with NaOH, it is converted to sodium phenoxide. Neutralisation of this salt gives phenol.



We have already mentioned the possible explanations of the low reactivity of aryl halides in earlier section. In above example, the chlorine atom in the C−Cl group is more tightly bound in Ar–Cl than in C−C−Cl because of the higher *s* character of sp^2 carbon of benzene ring. Another explanation was given that due to resonance,

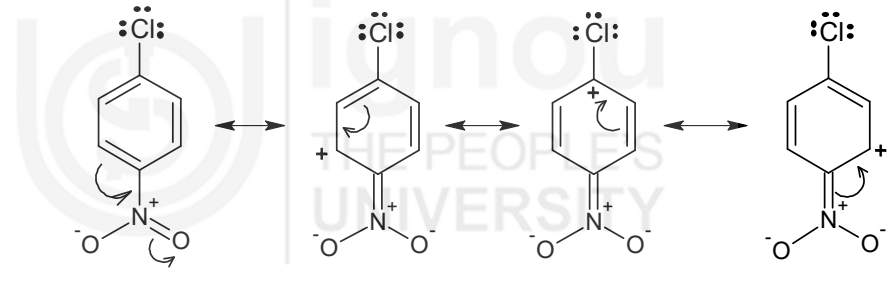
the carbon-halogen bond in aryl halides acquires partial double-bond character and hence the halogen atom is more strongly bound to carbon as compared to alkyl halides in which no resonance of this type exists. We also mentioned that electronegative halogen atom deactivates the benzene ring.

On the other hand, when a strong electron withdrawing group is present at *ortho* and/or *para* to the halogen atom in an aryl halide, the replacement of halogen by nucleophilic reagents is facilitated, e.g.



4-Nitrophenol (*p*-nitrophenol) **1-Chloro-4-nitrobenzene** (*p*-nitrochlorobenzene **4-Nitroaniline** (*p*-nitroaniline)

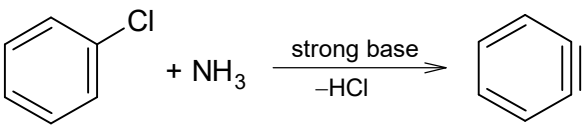
The resonance forms for the starting material (*p*-nitrochlorobenzene) indicate a low electron density at the halogen-bearing carbon. Similar forms can be written for the *o*-nitrochlorobenzene.



Resonance structure of 1-chloro-4-nitobenzene (*p*-nitrochloro**benzene)**

As shown above, the presence of nitro groups at *ortho*-position(s) and/or *para*-position withdraws the electron density from the benzene ring and thus creates intense positive charge on the carbon attached to chlorine. This facilitates the attack of the nucleophile on carbon attached to chlorine.

Nucleophilic aromatic substitutions do not follow S_N1 and S_N2 pathways. They occur by two different mechanisms: The **addition elimination mechanism** and the **benzyne intermediate mechanism**, which involves the highly reactive elimination reaction intermediate, **benzyne**.



Chlorobenzene **Benzyne**

The aromatic ring to which halogen is attached can undergo typical electrophilic aromatic substitution reactions, which we have already discussed in Units 11 and 12 . As you would recall, the halogen is deactivating and *ortho*, *para* directing. Now,

we will take up reactions of aryl halides in some more detail.

SAQ 4

Explain why the dipole moment of chlorobenzene is lower than that of chlorocyclohexane?

SAQ 5

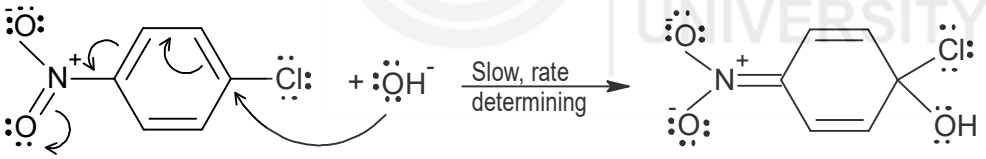
Write the resonating structures for 3-chloronitrobenzene. Compare these structures with 4-chloronitobenzene and give reason why nitro group at 3 position is not effecting reactivity of 3-chloronitrobenzene for nucleophilic substitution reactions?

14.4.1 Nucleophilic Substitution by Addition – Elimination

Now consider again the example of 1-chloro-4-nitrobenzene. When this compound is treated with aqueous sodium hydoxide (15 %), it is converted into 4-nitrophenol (*p*-nitrophenol). Such reactions occur in two steps: nucleophilic addition is followed by elimination. Step one is the slow and therefore it is rate determining step.

Mechanism: Nucleophilic Aromatic Substitution by Addition-Elimination

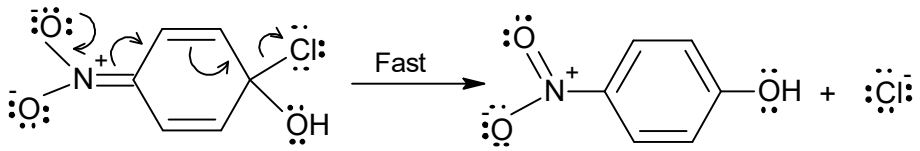
Step 1: Bond formation between hydoxide ion (a nucleophile) and carbon of C─ X bond (an electrophile)



A Meisenheimer complex

The intermediate complex is stabilized by a resonance interaction with nitro group. Such intermediates are named Meisenheimer complexes after the German Chemist who first characterised them. You can see how nitro group at *para* position is participating in delocalisation of the negative charge in the complex.

Step 2: Elimination of halide ion (leaving group) to regenerate aromatic ring and formation of phenol.

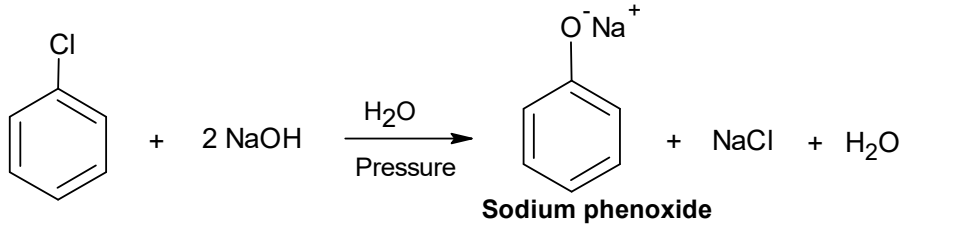


14.4.2 Nucleophilic Substitution *via* Benzyne Intermediate

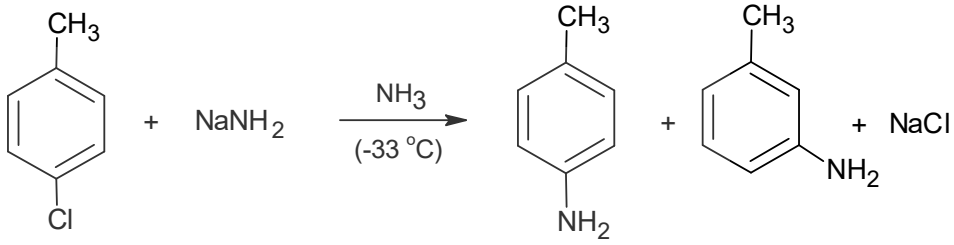
Aryl halides not having any strong electron withdrawing group at *ortho*- and

para- positions undergo nucleophilic substitution reaction *via* benzene intermediate.

Examples:



Sodium phenoxide

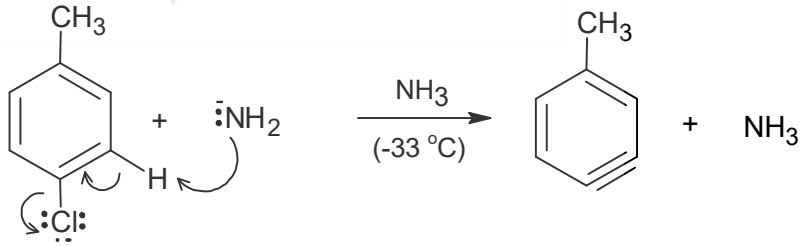


4-Methylaniline (*p*-toluidine) **3-Methylaniline** (*m*-toluidine)

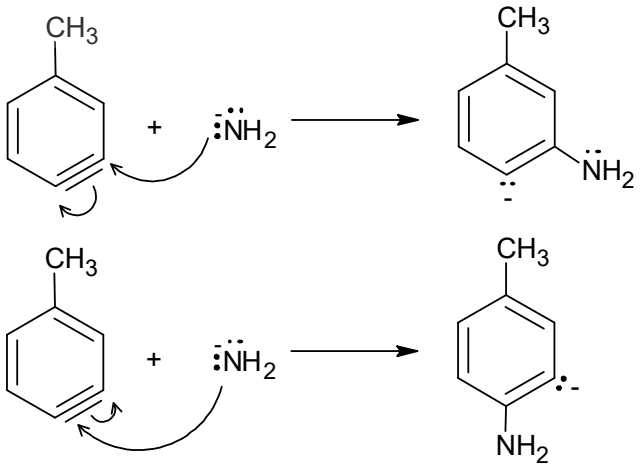
In second example you may have noticed that nucleophilic (NH_2^-) is not only attacking at the carbon centre of C—X bond but also at a position adjacent to it. To account for such experimental observation, it has been proposed that elimination of HX occurs to form a benzyne intermediate which then undergoes nucleophilic addition to the triple bond to give the products shown above.

Mechanism: Nucleophilic aromatic substitution *via* Benzyne Intermediate

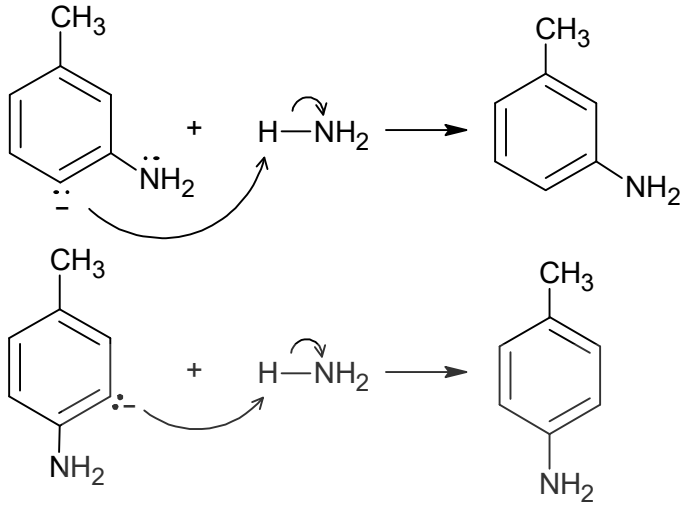
Step 1: Dehydrohalogenation of the benzene ring to form a benzyne intermediate.



Step 2: Amide ion (nucleophile) can attack both the carbon centres of triple bond to form two carbanion intermediates.

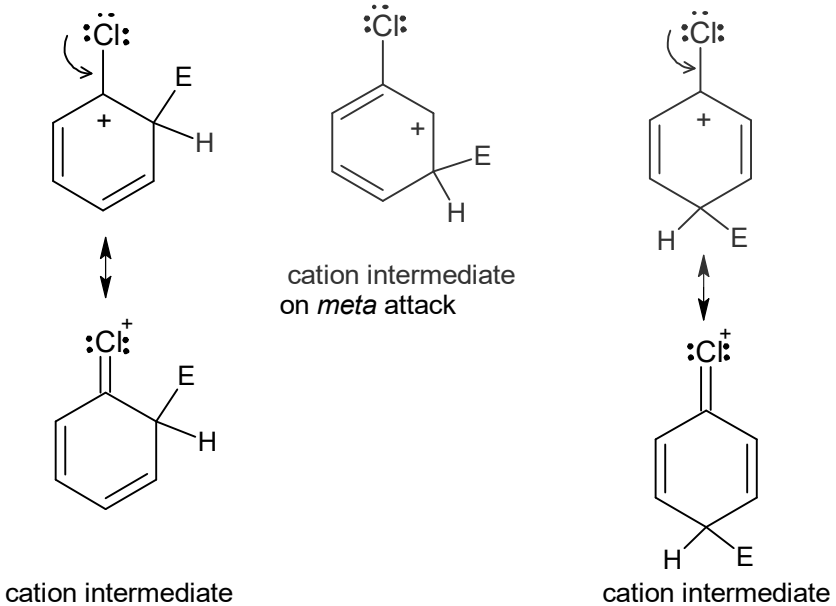


Step 3: Cabanions so formed abstract protons from ammonia to give final products.



14.4.3 Electophilic Substitution Reactions

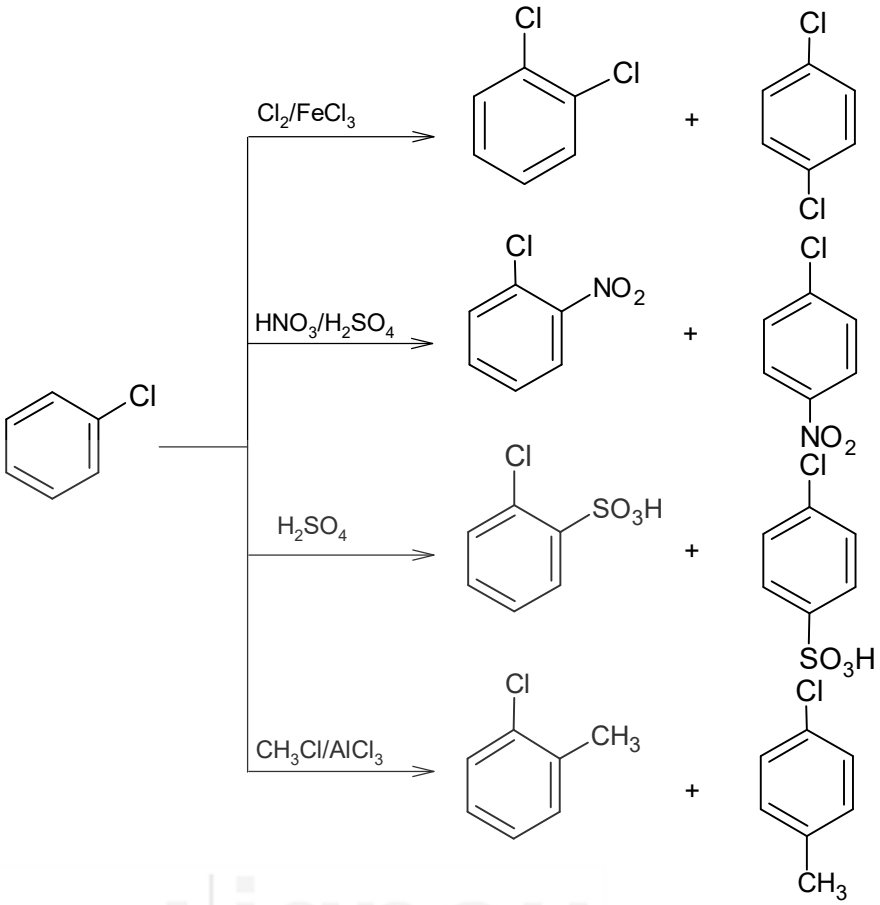
Similar to benzene, the benzene ring of chlorobenzene undergoes electrophilic aromatic substitution reaction. The most common electrophilic substitution reactions in chlorobenzene are halogenations, nitration, sulphonation and Friedel Crafts reaction. We have already discussed that chloro group in chlorobenzene is weakly deactivating and *ortho* and *para* directing. Because of this we need more drastic reaction conditions. *Ortho* and *para* directing orientation of chloro group for electrophilic aromatic substitution can be explained on the basis of the relative stability of carbocation intermediates formed by attack of electrophile on chlorobenzene. A chlorine *ortho* or *para* to the site of electrophilic attack can help to stabilise the carbocation intermediate by delocalization of the positive charge through resonance involving unshared electron pairs. Such stabilisation is not possible in carbocation intermediate formed on metra attack.



cation intermediate formed on *ortho* attack

cation intermediate on *meta* attack

cation intermediate on *para* attack

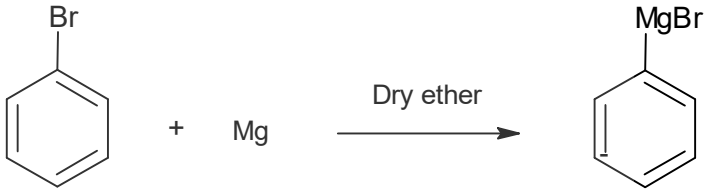


These reactions follow the mechanics discussed for the electrophilic addition reactions of benzene.

14.4.4 Reactions due to C−X Bond

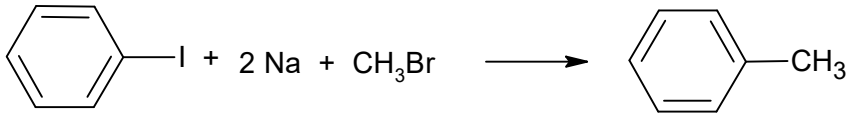
Besides the substitution reactions, aryl halides undergo reaction with metals to form organometallic compounds.

Bromo- and Iodobenzene: They react with magnesium metal to form Grignard reagents. Chlorobenzene is relatively unreactive.

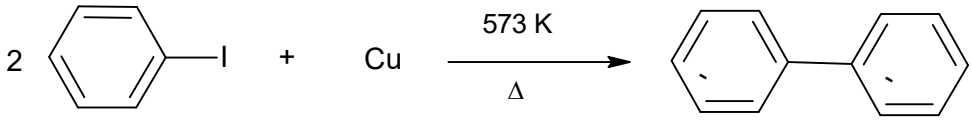


Phenylmagnesium bromide

Aryl halides react with alkyl halide in the presence of sodium metal to yield alkyl benzene. This reaction is known as Wutz- Fittig reaction. It is a modification of the Wurtz reaction which you have studied earlier.



Aryl halides on heating with copper powder give diaryls. This reaction is known as Ullmann reaction.



SAQ 6

How will you bring about the following conversions?

a) Iodobenzene to biphenyl.

b) Bromobenzene to phenylmagnesium bromide

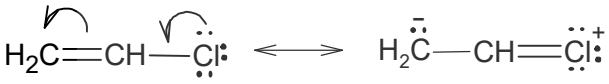
c) Benzene to 1-bromo-4-nitrobenzene

14.5 REACTIVITY AND RELATIVE STRENGTH OF C−X BONDS IN HALOGEN DERIVATIVES

Before taking up the reactivity and relative strength of C−X bond among halogen derivatives let us also understand the nature of alkenyl and alkynyl halides.

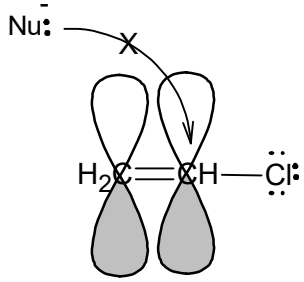
Alkenyl and alkynyl halides also similar to aryl halides and are less reactive towards nucleophilic substitution reactions and do not undergo S_N1 and S_N2 reactions.

In general, similar to aryl halides, C−X bonds are shorter and stronger in alkenyl and akynyl halides because i) in alkenyl halide, carbon attached to halogen is sp^2 hybridised and in alkynyl halide it is *sp* hybridised; ii) the C−Cl bond acquires partial double bond character due to resonance. As a result, the bond cleavage in alkenyl and alkynyl halide are difficult than alkyl halides and therefore, they are also less reactive towards nucleophilic substitution reaction. Both, alkenyl halides and alkynyl halides do not undergo $S_N1$and S_N2 reactions.



Resonating structures of chloroethene

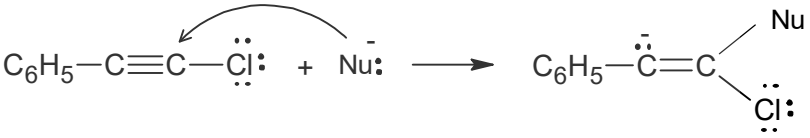
Lack of S_N1 and S_N2 reactivity of alkenyl halides and alkynyl halides can also be explained on the basis of the ease of formation of transition states. Because of the high *s* character of double and triple bonded carbons, they are stronger electron – attracting centres than saturated (sp^3) carbon, that is the reason alkyne and alkenes are stronger acids than alkanes. Therefore, it will be much more difficult to generate carbocations such as $CH_2 = CH^+$ and $HC \equiv C^+$ from the corresponding halides. Thus, this factor supports the lack of S_N1 reactivity of alkenyl and alkynyl halides. Further, *p* orbitals of carbon double and triple bond block the back side attack of nucleophile as shown below. This factor explains the lack of S_N2 reactivity in alkenyl and alkynyl halides.



Under drastic conditions, substitution of the halogens occurs in alkenyl and alkynyl halides. Such reactions follow different mechanism. In these cases, the nucleophile first adds to the carbon centre of C–X bond, and in a subsequent step the halogen leaves as halide ions. This is as "addition – elimination" mechanism.

Step 1:

Addition



Step 2:

Elimination

From our discussion on the nature and reactivity of alkyl, aryl, alkenyl and alkynyl halides, it can be concluded that the relative reactivity of halogen derivatives can be predicted on the basis following factors:

(i) *s* character of hybridised carbon attached to halogen

(ii) Resonance effect

(iii) Stability of carbocation formed on self ionisation od C−X bond (condition for S_N1 reaction)

(iv) Feasibility of back side attack on C−X bond (condition for S_N2 reaction)

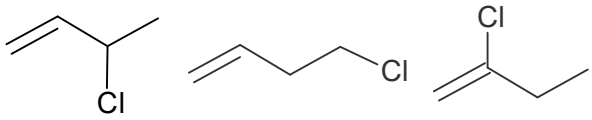
The C−X bond of alkenyl, alkynyl and aryl halide is shorter compared to alkyl halides because the carbon attached to halogen is either sp^2 or *sp* hybridised. Resonance effect also contributes in increasing bond strength of C−X in these compounds. Lack of stability of carboction, if formed, on self ionisation and lack of feasibility of backside attack of nucleophile on C−X bond explain that these compounds are less likely to follow S_N1 and S_N2 mechanisms.

In the Table 14.1 below, we have listed bond length and bond strength of each class of halogen derivatives.

Compound	C−X bond length (pm)	Bond Strength/kJ mol^{-1}
C_2H_5– Cl	177	340
CH_2 = CH– Cl	169	435
HC≡ C– Cl	163	--
C_6H_5 – Cl	169	465

SAQ 7

Arrange following halides in order of expected increasing reactivity towards sodium iodide.



14.6 SUMMARY

In this unit, we have described the chemistry of aryl halides. We are summarizing below what we have studied:

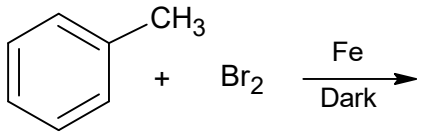
- Aryl halides can be prepared from aromatic hydrocarbons by direct halogenation and form amines by forming diazonium salt.
- Aryl halides are not as reactive as alkyl halides for nucleophilic substitution reactions. They may react with moderate base such as NaOH at high temperature and high pressure or with very strong base such as $NaNH_2$.
- Aryl halides are activated by presence of *ortho* and/or *para* strong electron withdrawing groups.

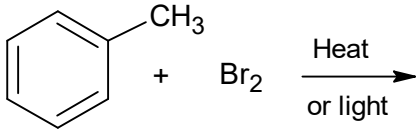
  Nucleophilic aromatic substitutions in ary halides do not follow S_N1 and S_N2 pathways. These reactions occur by two different mechanisms: The addition-elimination mechanism and the benzyne intermediate mechanism.

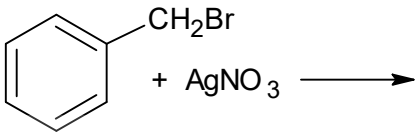
  The aromatic ring to which halogen is attached can undergo typical electrophilic aromatic substitution reactions. Halogen group is deactivating and *ortho*, *para* directing.
- Aryl halides react with magnesium to form aryl magnesium halides called the Grignard reagents.

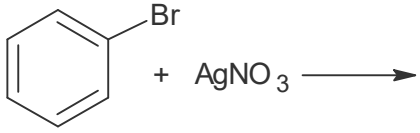
14.7 TERMINAL QUESTIONS

1. Complete the equation for each of the following reactions. Write only major monohalogen substituted product in each case.

a) 

b) 

c) 

d) 

2. Which of the following compounds undergo S_N2/S_N1 reaction? Explain.

   a) Benzyl chloride;

   b) Chlorobenzene;

   c) Chloroethene;

   d) Chloroethyne.

3. Write the equation for each of the following reactions:

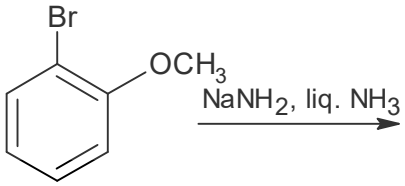
   a) 2,4-dinitrochlorobenzene and sodium hydroxide

   b) 2,4-dinitrochlorobenzene and sodium phenoxide

   c) 2,4-dinitrochlorobenzene and ammonia

   d) Chlorobenzene and sodium amide (sodamide).

4. In the following reaction only *meta* isomer is formed though this reaction undergoes benzyne mechanism. Explain.



5. Although chlorine is an electron withdrawing group, yet it is *ortho*-, *para*-directing in electrophilic aromatic substitution reactions. Why?

6. What happens when?

   (i) Iodobenzene is heating with copper powder,

   (ii) bromobenzene is heated with Mg,

   (iii) chlorobenzene is subjected to hydrolysis,

(iv) Chlorobenzene is treated with alkyl halide in the presence of sodium metal,

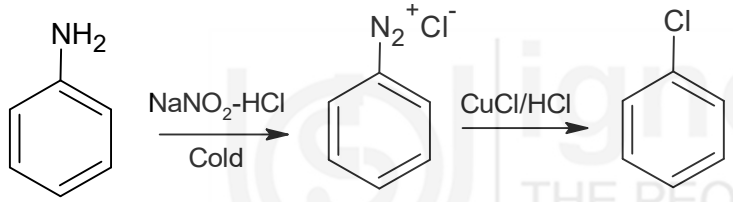
14.8 ANSWERS

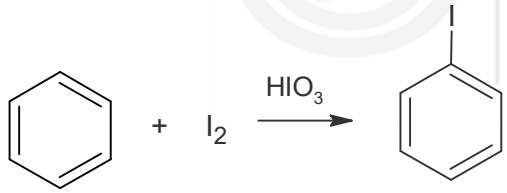
Self Assessment Questions

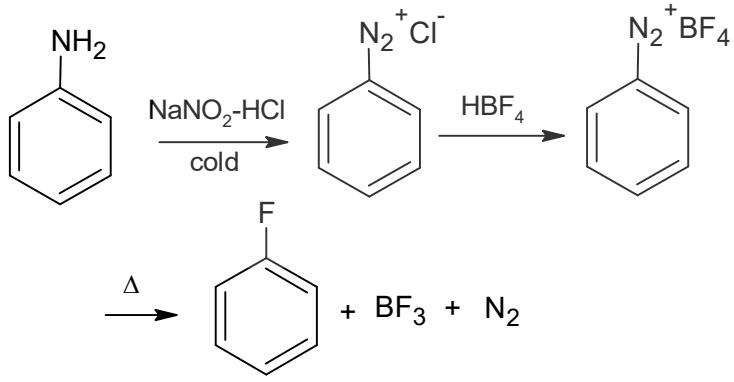
1. The carbon-halogen bond in aryl halides is shorter and stronger than C—X bond of alkyl halide because of the (i) carbon atom of C—X bond is sp^2 hybridized (having higher *s* character), (ii) resonance effect causes partial double bond character in C—X bond. Therefore, it is difficult to break during substitution reaction. Few more factors for low reactivity of aryl halide are: poor bond polarity of C—X bond, unfavorable geometry for back side attack of nucleophile due to benzene ring and difficulty in generation of phenyl cation.

2. There are two main reason beside C—X bond strength: (i) formation of phenyl cation in case of aryl halides is difficult (S_N1 condition is not fulfilled), (ii) Back side attack on C—X carbon by nucleophile is not possible because of the electron rich aromatic ring (S_N2 condition is not fulfilled).

3.

a) 

b) 

c) 

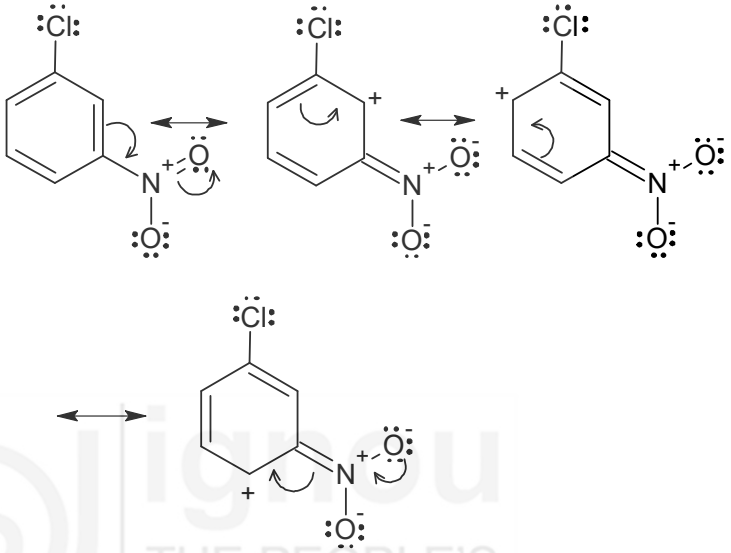
4. There are two main factors which are responsible for the lower dipole moment for the C—Cl bond in chlorobenzene than the dipole moment of the same bond in cyclohexyl chloride:

   i) In chlorobenzene, the carbon attached to chlorine is sp^2 hybridized, on the other hand, in cyclohexyl chloride it is sp^3 hybridized. Because of the higher *s* character of sp^2 carbon, it is more

electronegative than sp^3 carbon and hence it has fewer tendencies to release electron to chloride atom. This in turn will make the dipole moment weaker when we compare with sp^3 hybridized C−Cl bond.

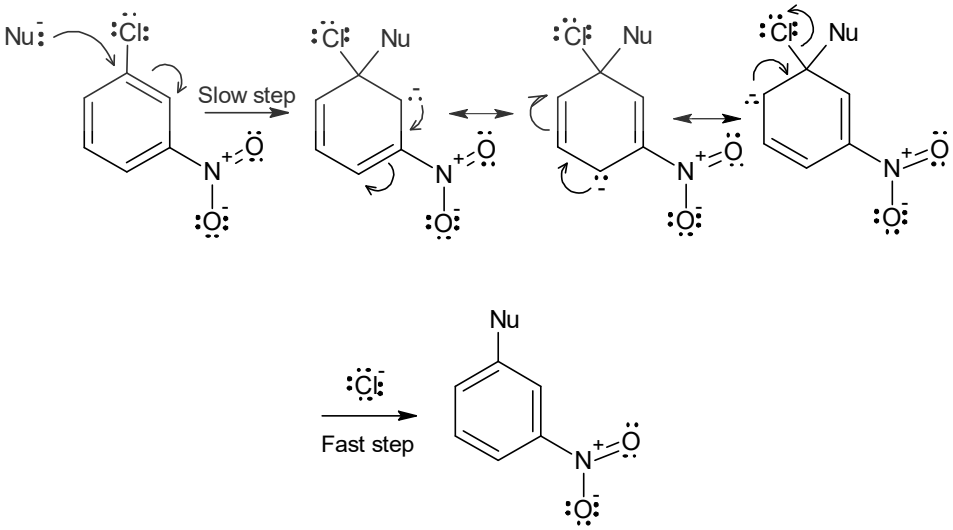
ii) Delocalisation of lone pairs of electrons of chlorine atom over the benzene ring causes partial double bond character in C−X bond. Thus, the C−X because of resonance effect is shorter than single bond. The bond length has a direct impact on dipole moment because dipole moment depends on charge and distance.

5. Resonance structures of 1-chloro-3-nitrobenzene:

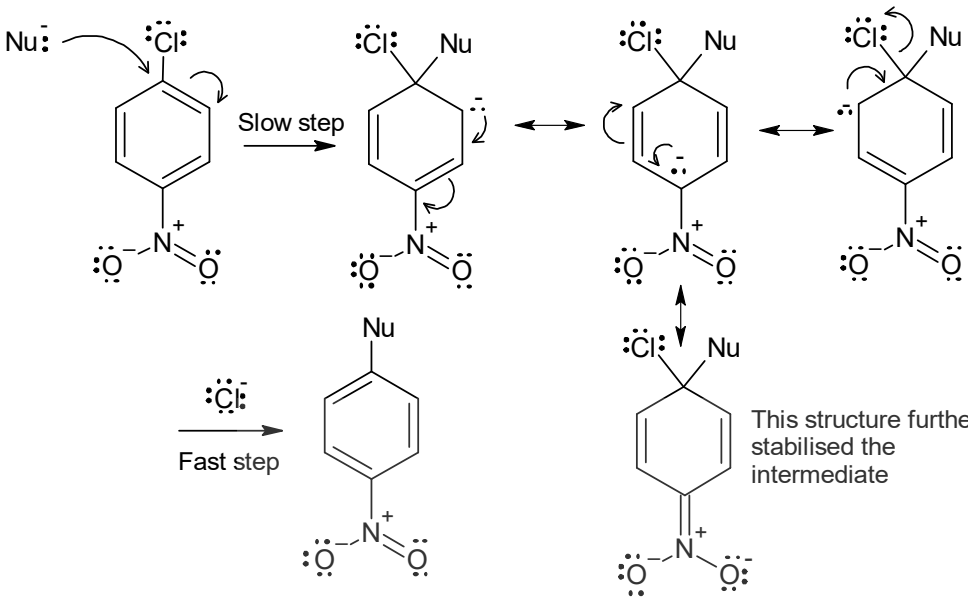


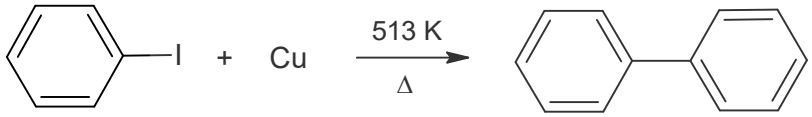
None of the resonating structure bear the +ve charge on carbon atom attached to the −Cl group. But you can see presence of nitro group at 4 position withdraw the electron density from carbon attached to Chlorine atom (See resonance structure III, Sec. 14.4). Further the transition state formed by the attack of a nucleophile is stabilised by the nitro group while in case of 3-chloronitrobenzene, none of the resonating structure bear the negative charge on carbon bearing the $-NO_2$ group.

Nucleophilic attack on 1-chloro-3-nitobenzene

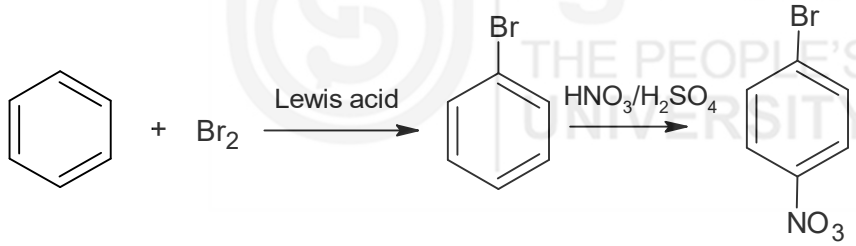


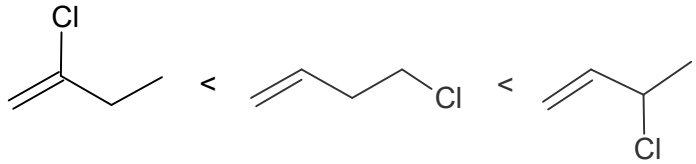
Nucleophilic attack on 1-chloro-4-nitobenzene



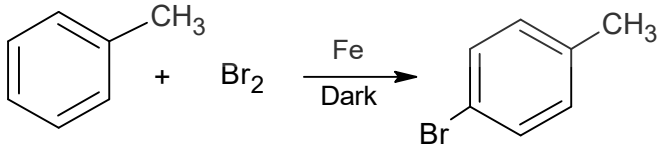
6. a) 

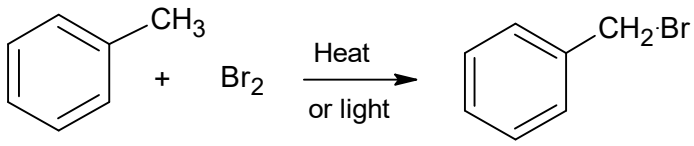
b) 

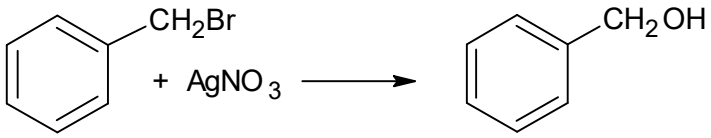
c) 

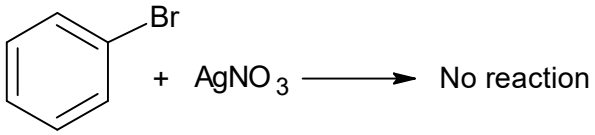
7. 

Terminal Questions

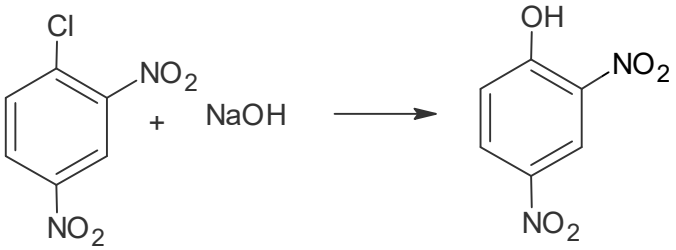
1. a) 

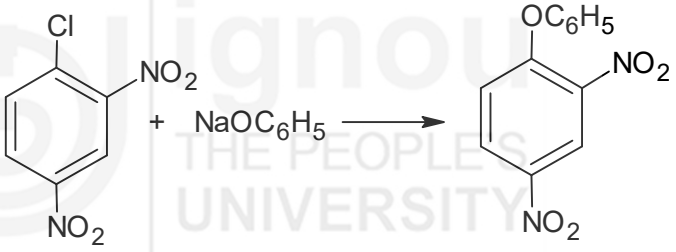
b) 

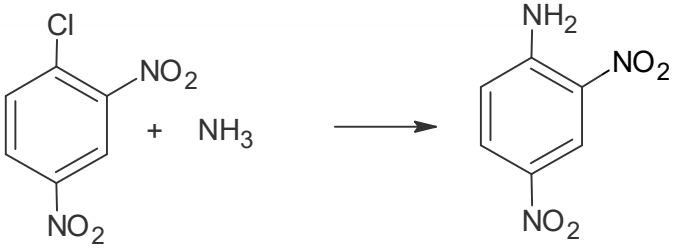
c) 

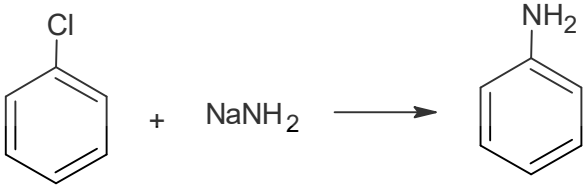
d) 

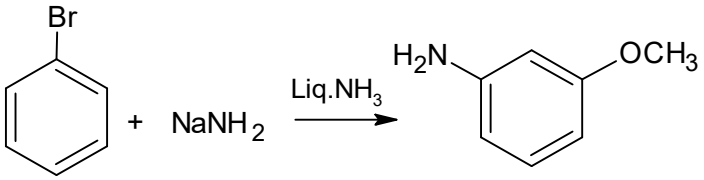
2. Formation of carbocations and back side attacks of nucleophile in the case of chlorobenzene, chloroethene and chloroethyne are not feasible, therefore they will not go for S_N1 and S_N2 reactions. On the other hand in benzyl chloride, benzene ring contributes in stabilisation of both carocation and transition state of S_N2 reaction formed during S_N1 and S_N2 reactions. So benzyl chloride will go for S_N1/S_N2 reaction.

3. a) 

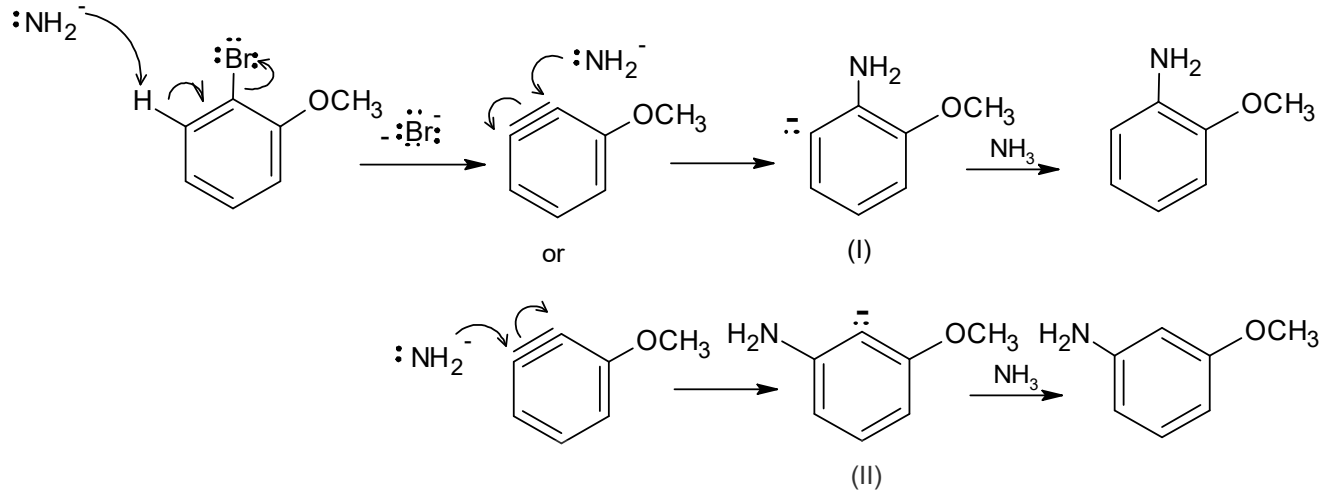
b) 

c) 

d) 

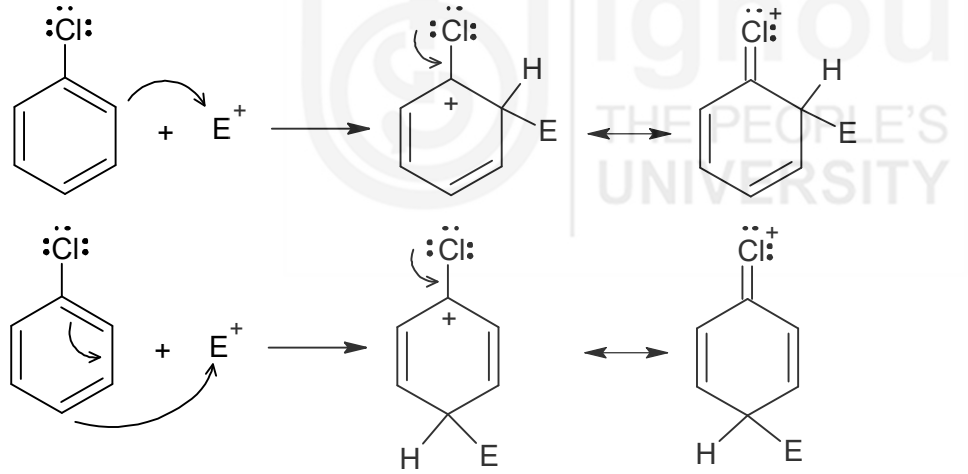
4. 

Consider the mechanism of the reactions.

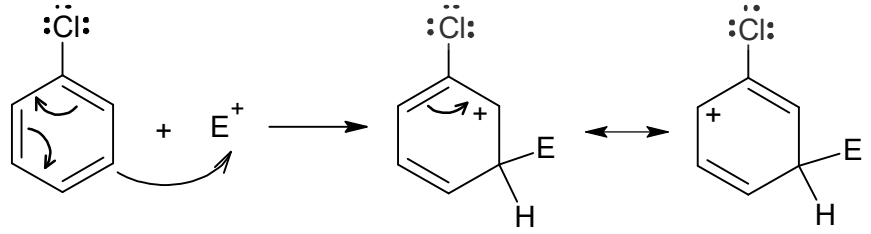


The carbanion (II) formed after amide addition to the intermediate benzyne is stabilised by the electron-withdrawing effect of the methoxy, therefore it is formed regio-selectively. Thus, in this reaction, only one product, i.e. 3-methoxyaniline (*m*-anisidine) is formed.

5. In chlorobenzene, Inductive effect deactivates the benzene ring, but it is *ortho* and *para* directing for electrophilec substitution reactions because of the resonance effect. Carbocation formed after electrophilc attack is more stabilised when it is attacked by an electrophile on *ortho* or *para* position.



Above shown contribution of chlorine atom in resonance stabilisation is not feasible for *meta* attack.



6. i) biphenyl is formed

   ii) phenylmagnesium bromide is formed

iii) at normal temperature there is no reaction but on heating at 573 K and at pressure 238 atom with aqueous NaOH it forms phenol.

iv) alkylbenzene is formed.