UNIT 17

ALKYL HALIDES

Learning Outcomes:

After studying this unit and working the exercise the student will be able to,

- Name alkyl halides using IUPAC system.
- Discuses the structure and reactivity of RX.
- Describe the preparation of RX by the reaction of alcohols with HX, $SOC\ell_2$ and PX_3 and by radical halogenation of alkanes.
- Describe the mechanism and types of nucleophilic substitution reactions.
- Describe the mechanism and types of elimination reactions.
- Discuss chemistry of Grignard reagents by the addition of aldehydes, ketones, esters and carbon dioxide.
- Discuss nomenclature, structure and basicity of amines.
- Describe the preparation of amines by alkylation of ammonia with RX and reduction of nitriles, nitro and amide functional groups.
- Describe the chemistry of amines by alkylation of amines with RX, reactions with aldehydes, ketones preparation of amines and diazonium salts.
- Describe isomerism of alkyl halides and amines.

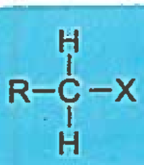
17.1 Alkyl Halides:

Monohaloalkanes are usually called alkylhalides. Alkyl halides are the compounds of carbon, hydrogen and halogen. The functional group of these compounds is halogen. These are the derivatives of alkanes in which one hydrogen atom is replaced by a halogen atom.

$$R-X$$

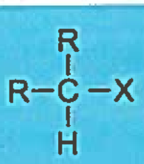
They are represented by $R-X$, where R is an alkyl group and "X" is functional group. The general formula of alkylahlides is $C_nH_{2n+1}X$ where n represents the number of carbon atoms.

Alkyl halides are classified as primary, secondary and tertiary alkylhalides depending upon whether the halogen atom is directly bonded to a primary, secondary or tertiary carbon atom in the molecule. For example.



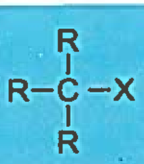
$$\begin{array}{ccc} & H & \\ & | & \\ R- & C & -X \\ & | & \\ & H & \end{array}$$

Pri-alkylhalide



$$\begin{array}{ccc} & R & \\ & | & \\ R- & C & -X \\ & | & \\ & H & \end{array}$$

Sec-alkylhalide



$$\begin{array}{ccc} & R & \\ & | & \\ R- & C & -X \\ & | & \\ & R & \end{array}$$

Ter-alkylhalide

Alkyl halides are the most suitable organic compounds used to incorporate alkyl groups into other molecules.

17.1.1 Nomenclature of Alkyhalides:

Common System: According to this system the names of alkylhalides are two word names. In this two word names, the alkyl group of alkylhalide is named first followed by the name of halogen group as halide.

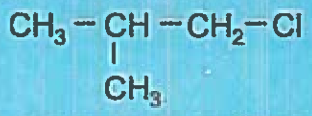
$CH_3-C\ell$ (Methylchloride) CH_3-CH_2-I (Ethyliodide)

In case of primary, secondary and tertiary alkyl halides, the words pri, sec, and ter are written before the names of alkyl halides.

IUPAC System:

Rules:

1. Selection of the longest continuous chain of carbon atom containing the halogen atom.
2. Derivation of the basic name by writing the word halo before the name of alkane from which the alkylhalide has been derived. The basic name becomes as a Haloalkane.
3. Numbering of the carbon atoms of the selected chain from the end nearer to halogen group.
4. Naming all the other substituents and indication of their positions by appropriate numbers.



$$CH_3-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_2-Cl$$

1-Chloro - 2 - methyl propane

17.1.2 Physical Properties of Alkyl halides:

Lower alkyl halides $CH_3C\ell$, $C_2H_5C\ell$ and CH_3F are gases at room temperature. Alkyl halides upto C_{18} are colorless liquids while those beyond

C_{18} are colourless solids. They are usually insoluble in water due to their inability to form hydrogen bonding with water. They are soluble in organic solvents. Alkyl chlorides and alkylflourides are lighter than water while alkyl iodides and alkyl bromides are denser than water. They have higher boiling points than the corresponding alkanes. For a given alkyl group the boiling points of alkyl halides increase with increasing size of the halogen atom while for a given halogen atom the boiling points of alkylhalides increase with the increasing size of the alkyl group.

Table 7.1: Boiling Points of Alkyl halides:

Name	Structure	Boiling Point °C
Methyl chloride	$CH_3-C\ell$	–24
Methyl bromide	CH_3-Br	5
Methyl iodide	CH_3-I	40
Ethyl chloride	$CH_3-CH_2-C\ell$	13
Ethyl bromide	CH_3-CH_2-Br	38
Ethyl iodide	CH_3-CH_2-I	72

17.1.3 Structure of Alkyl Halides:

To understand the structure of alkyl halides, let us consider methyl chloride $(CH_3C\ell)$. In this molecules all the bonds of carbon are single, therefore, carbon atom is sp^3 – hybridized. During the process of bond formation, one sp^3 orbital of carbon atom overlaps with the half filled p–orbital of chlorine atom and forms a single "δ" covalent bond. In the meantime the remaining three sp^3 orbitals of this carbon atom overlap with three half filled s-orbitals of hydrogen atoms and forms single "δ" covalent bonds. The H−C−H and H−C−X bond angles are approximately equal to 109.5 °.

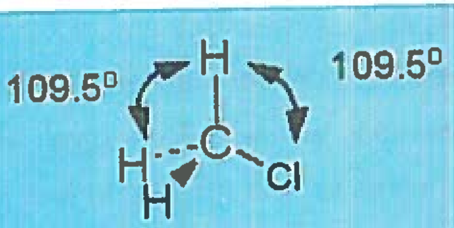


Fig: 17.1

17.1.4 Preparation of Alkyl Halides:

Alkyl halides can be prepared by different methods. Some of these are given as under.

17.1.4.1 Reaction of halogen acids with alcohols

Alcohols readily react with HBr and HI to form alkylbromides and alkyliodides. HCl is least reactive towards alcohols, therefore, anhydrous $ZnCl_2$ is used as catalyst while treating alcohol with HCl to produce alkyl chlorides ($ZnCl_2$/HCl is called Lucas reagent).

$$\underset{\text{Alcohol}}{R-OH} + \underset{\text{Halogen acid}}{H-X} \longrightarrow \underset{\text{Alkylhalide}}{R-X} + H_2O$$

$$\underset{\text{Ethylalcohol}}{CH_3-CH_2-OH} + H-Br \longrightarrow \underset{\text{Ethylbromide}}{CH_3-CH_2-Br} + H_2O$$

$$\underset{\text{Ethyl alcohol}}{CH_3-CH_2-OH} + H-I \longrightarrow \underset{\text{Ethylchoride}}{CH_3-CH_2-I} + H_2O$$

$$CH_3-CH_2-OH+H-C\ell \xrightarrow{Anh.(ZnC\ell_2)} CH_3-CH_2-C\ell+H_2O$$

Ethyl alcohol Ethylchloride

17.1.4.2 (a) By the action of Phosphorous Halides on Alcohols:

Alcohols react with phosphorous trihalides $(PC\ell_3, PBr_3)$ and form the corresponding alkyl halides.

$$3R-OH+PX_3 \longrightarrow 3R-X+H_3PO_3$$

Alcohol Alkylhalide

$$3CH_3-OH+PCl_3 \longrightarrow 3CH_3-Cl+H_3PO_3$$

Methylalcohol Methylchloride

$$3CH_3-CH_2-OH+PI_3 \longrightarrow 3CH_3-CH_2-I+H_3PO_3$$

Ethylalcohol Ethyliodide

$$3CH_3-CH_2-OH+PBr_3 \longrightarrow 3CH_3-CH_2-Br+H_3PO_3$$

Ethylalcohol Ethylbromide

Phosphorous trihalides are produced in situ by the action of red phosphorous on halogen.

(b) By The Action of Thionylchloride on Alcohols:

Alcohols react with thionylchloride $(SOCl_2)$ in the presence of pyridine to yield the corresponding alkyl halides. Pyridine being a base absorbs $HC\ell$ just after its production in the reaction mixture.

$$R-OH \quad + \quad SOCl_2 \xrightarrow[-HCl]{Pyridine} R-Cl+SO_2$$

Alcohol — Thiony chloride — Alkyl halide

$$CH_3-OH+SOCl_2 \xrightarrow[-HCl]{Pyridine} CH_3-Cl+SO_2$$

Methyl alcohol — Methyl chloride

$$CH_3-CH_2-OH+SOCl_2 \xrightarrow[-HCl]{Pyridine} CH_3-CH_2-Cl$$

Ethyl alcohol — Ethyl chloride

17.1.4.3 By Free Radical Halogenations of Alkanes:

Alkanes react with halogens in the presence of ultraviolet (uv) light or at high temperature of about 400°C to yield alkyl halides. In this process one or more hydrogen atoms of alkanes are replaced by halogens giving a mixture of different alkyl halides. That is why it is not a good method for preparation of pure alkylhalides.

$$R-H+C\ell_2 \xrightarrow[400^{\circ}C]{uv} R-C\ell+HC\ell$$

This reaction occurs through free radical mechanism.

17.1.5 Reactivity of Alkyl halides:

The bond between carbon and halogen of alkyl halides is reactive due to its polar nature $(C^{+\delta}-X^{-\delta})$. The polarity is due to higher electronegativity of halogen than carbon atom. Due to this polarity the carbon atom of alkyl halide is a good and attractive target for the attack of a nucleophile. That is why allyl halides are considered as a reactive group of organic compounds. These are widely used for the synthesis of a large variety of organic compounds.

The strength of carbon –halogen bond $(C-X)$ decreases down the group from fluorine to iodine. This can be explained on the basis of their bond energies that are given in the table.

$C-X$ Bond	Bond Energy $(kJ\,.\,mol^{-1})$
$C-F$	467
$C-Cl$	346
$C-Br$	290
$C-I$	228

This shows that iodo compounds are most reactive while floro compounds are least reactive. Therefore, the order of reactivity of alkyl halides is $R-I > R-Br > R-C\ell > R-F$.

17.1.6 Nucleophilic Substitution Reactions:

17.1.6.1 General introduction: Alkyl halides undergo nucleophilic substitution reaction in which a stronger attacking nucleophile replaces the halogen of alkyl halide as halide ion $(\bar{X})$. A general example of such a reaction is given as

$$\underset{\text{Substrate}}{CH_3-X} + \underset{\substack{\text{Attacking}\\\text{Nucleophile}}}{\overset{\bar{\cdot\cdot}}{Nu}} \longrightarrow \underset{\text{Product}}{CH_3-Nu} + \underset{\substack{\text{Leaving group}\\\text{or}\\\text{Nucleofuge}}}{\bar{X}}$$

17.1.6.2 Important Concepts

17.1.6.2.1 Carbocations and their Stability:

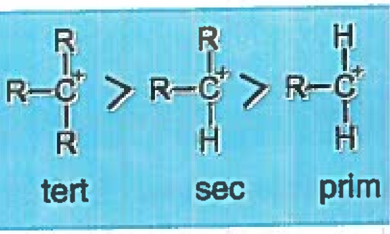
When halogen atom detaches from the carbon atom of an alkyl halide as halide ion $(\bar{X})$, the substrate is converted into a positively charged ion. This ion in which carbon atom bears positive charge is known as carbocation or carbonium ion.

$$(R)_3C-Br \rightarrow (R)_3C^+ + Br^- \quad \Delta H = 149 kcal/mol$$

$$(R)_2CH-Br \rightarrow (R)_2CH^+ + Br^- \quad \Delta H = 163 kcal/mol$$

$$RCH_2-Br \rightarrow R-CH^+ + Br^- \quad \Delta H = 182 kcal/mol$$

There are three types of carbocations. Primary alkyl halides produce primary carbocations while secondary and tertiary alkyl halides yield secondary and tertiary carbocations.



$$R-\overset{R}{\underset{R}{C^+}} > R-\overset{R}{\underset{H}{C^+}} > R-\overset{H}{\underset{H}{C^+}}$$

Tertiary carbocations are more stable than secondary and secondary are more stable than primary ones. This stabilization comes from the stabilization of the positive charge of carbocation by the electron donating alkyl groups directly attached. Greater the number of alkyl groups, greater is the stability of the carbocation.

17.1.6.2.2 Nucleophile and Base:

Nucleophile means nucleus lover. It is a species which donates a pair of electrons in a chemical reaction.

It attacks the regions of low electron density e.g. positive centre in the molecule of substrates. They may be negative ions or neutral species with lone pair of electrons.

A nucleophile is generally represented by $N\bar{\ddot{u}}$. Any species neutral or negatively charged with a lone pair of electrons can act both as a base and a nucleophile. But a base is a species which has affinity for proton whereas a nucleophile has the ability to form bond with carbon atom. A base attacks a hydrogen atom in the elimination reaction while a nucleophile attacks carbon atom in the substitution reactions.

Mechanisms of Nucleophilic substitution Reactions or (SN Reaction):

Alkyl halides undergo nucleophilic substitution (SN) reactions by two different types of mechanisms. The type of mechanism depends upon the nature of alky halides. Tertiary alkyl halides undergo unimolecular nucleophilic substitution (SN^1) while primary alkyl halides undergo bimolecular nucleophilic substitution (SN^2).

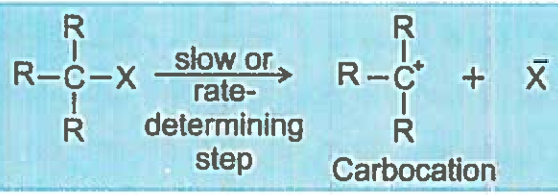
17.1.6.2.3 Substrate and leaving group:

The molecule which undergoes nucleophilic substitution reaction is called substrate. In this case alkyl halides are substrates.

The group or species which leaves the substrate or which is being replaced by the incoming entering group is called leaving group. It is also called nucleofuge. In this reaction halogen leaves the substrate as halide ion $(\bar{X})$.

17.1.6.3 SN^1 –Mechanism:

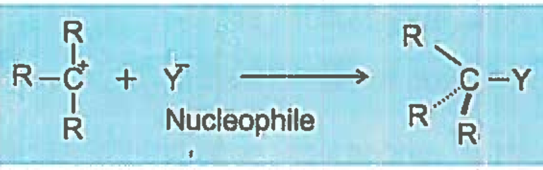
SN^1 stands for unimolecular nucleophilic substitution reaction. SN^1 reactions are defined as those nucleophilic substitution reactions in which only one molecule is involved in the rate determing or slow step of the reaction. These reactions are generally followed by tertiary alkyl halides in polar solvents. These reactions complete in two steps. In first step, the substrate undergoes ionization and yields a carbocation. The halogen atom completely detaches from the substrate as halide ion $(\bar{X})$.



$$R_3C-X \xrightarrow[\text{rate-determining step}]{\text{slow or}} \underset{\text{Carbocation}}{R_3C^+} + \bar{X}$$

This is the slow or rate determining step of the reaction because it involves dissociation of substrate. Since only one molecule (substrate) is involved in this rate determining step this reaction is called unimolecular nucleophilic substitution reaction (SN^1).

In the second step the entering nucleophile attacks the carbocation to produce the end product.



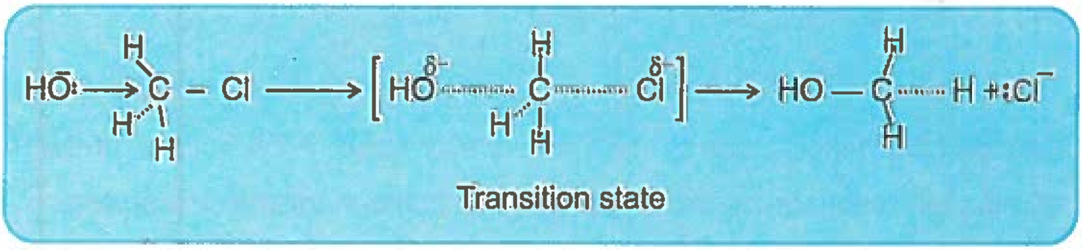
This is the fast step of the reaction because it involves the ions. The kinetic studies have shown that reactions proceeding through SN^1 – mechanism follow the first order kinetics. The rate of reaction depends only upon the concentration of substrate. The rate equation is

$$\text{Rate} = K[(R)_3C-X]$$

17.1.6. 4 SN^2 –Mechanism:

SN^2 stands for bimolecular nucleophilic substitution reaction. SN^2 reactions are defined as those nucleophilic substitution reactions in which two species are involved in the rate determing or slow step of the reaction. This mechanism is generally followed by primary alkyl halides in non – polar solvents. These reactions are completed in one step only.

The attacking nucleophile attacks the electrophilic carbon atom of the substrate before the leaving group departs. The entering group can attack only from the back side because the front side is blocked by the halogen atom. As the reaction proceeds the bond between the entering group and substrate starts to form and the bond between the leaving group and substrate weakens. A transition state is formed in which both the entering and leaving groups are partially bonded to the carbon atom of the substrate. In other words, the extent of bond formation on one side is equal to the extent of bond breaking on the other side.



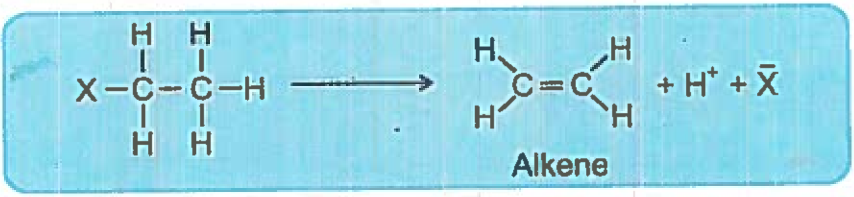
Finally, the bond between the leaving group and substrate is completely broken while the bond between the entering group and substrate is formed completely.

Primary alkyl halides undergo SN^2 and tertiary alkyl halides undergo SN^1 mechanism. The type of mechanism followed by the secondary alkyl halides is governed by the nature of the solvent. If polar solvent is present, they follow SN^1 mechanism while in non polar solvents they follow SN^2 mechanism.

17.1.7 Elimination Reactions:

17.1.7.1 Overview:

Elimination reactions are those reactions which involve the elimination or removal of atoms or group of atoms from two adjacent carbon atoms in the substrate molecule to form a multiple bond. These are the reverse of addition reactions. During elimination reactions two strong sigma (δ) bonds are broken down and a new weaker Pi(π) bond is formed. The saturated compounds are converted to unsaturated compounds. In the molecules of alkyl halides, during elimination, a hydrogen and halogen are removed from adjacent carbon atoms resulting in the conversion of alkyl halide to alkene. For example

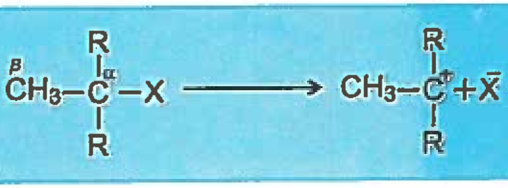


The reaction takes place in the presence of base. Alkyl halides undergo elimination reactions by two different types of mechanisms. These are:

17.1.7.2 E^1 – Mechanism:

E^1 stands for unimolecular elimination reactions. In these reactions only one molecule e.g. substrate is involved in the rate determining or slow step. These reactions, therefore, follows first order kinetics. These reactions are usually followed by tertiary alkyl halides which are completed in two steps, like SN^1 reactions.

In the first step, substrate ionizes and forms a tertiary carbocation. Halogen leaves as halides ion $(\bar{X})$.



$$\overset{\beta}{CH_3}-\overset{\overset{R}{|}}{\underset{\underset{R}{|}}{\overset{\alpha}{C}}}-X \longrightarrow CH_3-\overset{\overset{R}{|}}{\underset{\underset{R}{|}}{C^+}}+\bar{X}$$

This step involves the breaking of bond, therefore, it is the slow step or rate determining step of the reaction. In the second step, the base removes a hydrogen atom from the β−carbon atom of the carbocation as proton. This results in the formation of a double bond between α and β carbon atoms. The end product is an alkene

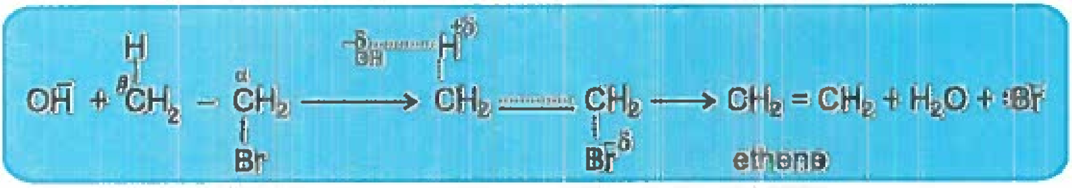
The rate equation for E^1 reactions is

$$\text{Rate} = k[R-X]$$

17.1.7.3 E^2 –Mechanism:

E^2 stands for bimolecular elimination reaction. Two species i.e. substrate and base are involved in the rate determining step of these reactions. These reactions follow second order kinetics therefore, their molecularity is two. E^2 reactions are generally followed by primary alkyl halides and are completed in one step like SN^2 reactions.

The removal of proton from the $\beta-$carbon atom by a base and the removal of halide ion $(\overline{X})$ from the $\alpha-$carbon atom of the substrate takes place simultaneously. For example



$$\overset{-}{OH} + \underset{}{\overset{\overset{H}{|}}{\overset{\beta}{C}H_2}} - \underset{\underset{Br}{|}}{\overset{\alpha}{C}H_2} \longrightarrow \overset{\overset{\delta-}{BH}\cdots\cdots\overset{\delta+}{H}}{\overset{|}{CH_2}}\cdots\cdots\underset{\underset{Br^{\delta-}}{|}}{CH_2} \longrightarrow \underset{\text{ethene}}{CH_2=CH_2} + H_2O + :\overline{Br}$$

The rate equation of E^2 reactions is

$$\text{Rate} = k[\text{Substrate}][\text{Base}]$$

17.1.8 Substitution Versus Elimination:

As all the bases are also nucleophiles, the competition between substitution and elimination reactions is determined by the fact whether it is a better base or a better nucleophile. A stronger base will favour in elimination while a stronger nucleophile will favour substitution in the same substrate. For example 2–bromopropane on reaction with ethoxide undergoes elimination and produces alkene as the major product because ethoxide is a strong base. On the other hand the same 2–bromopropane on reaction with an anion of the corresponding thioalcohol ($C_2H_5S^-$) undergoes substitution reaction because $C_2H_5S^-$ is more nucleophilic and less basic than $C_2H_5O^-$.

Crowding within the molecule of substrate also generally favours elimination over substitution reaction. This is due to the greater steric hindrance when the nucleophile approaches towards α carbon atom of the substrate. The greater number of alkyl groups on the substrate favours elimination over substitution because these alkyl group stabilize alkene more than the substitution product.

17.2 Organometallic Compounds (Grignard Reagents):

All those organic compounds which contain at least one carbon–metal bond in their structures are known as organometallic compounds.

$$R-M$$

Where $M = Mg, Li, Pb, Zn$ etc.

They are named simply by adding the name of the metal to the organic group bonded directly to the metal. For example,

CH_3-MgI	$(CH_3)_4Pb$
Methylmagnessium iodide	Tetramethyllead

Alkyl or aryl magnesium halides are commonly known as Grignard reagents. They were discovered, prepared and studied by victor Grignard, therefore, they were named after him as Grignard reagents. They are highly reactive organic compounds. They are used in the synthesis of a large number of alkanes, alkynes, alcohols, aldehydes, ketones, carboxylic acids etc. Due to this great achievement Grignard was awarded with Noble Prize in 1912. The general formula of Grignard reagents is R–MgX where R represent Alkyl group and X represent Halogen atom (Cl, Br, I).

Examples are

$$CH_3-Mg-Br$$
$$CH_3-CH_2-Mg-Cl$$

17.2.1 Preparation of Grignard Reagents:

Grignard reagents are prepared in the laboratory by the action of alkyl or aryl halides on freshly prepared magnesium metal in the presence of anhydrous or dry ether.

$$R-X+Mg\xrightarrow{\text{Ether}}R-MgX$$

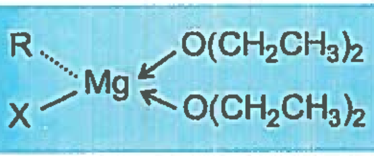
This reaction takes place in two steps. In the first step alkyl halide reacts with magnesium and yields alkyl radical and an $\dot{\text{M}}\text{gX}$ type of species.

$$\underset{\text{Alkylhalide}}{R-X} \quad + \quad Mg\xrightarrow{\text{1st Step}}\underset{\text{Alkyl Radical}}{\dot{R}} \quad + \quad \dot{\text{M}}\text{gX}$$

In the second step, $\dot{R}$ combines with $\dot{\text{M}}\text{gX}$ and yields the Grignard reagent

$$\dot{R}+\dot{\text{M}}\text{gX}\xrightarrow{\text{2nd Step}}\underset{\text{Grignard Reagent}}{R-MgX}\cdot$$

Diethyl ether used in the preparation of Grignard reagent plays two important roles. At one hand it provides a medium (Solvent) for the reaction, at the other hand it dissolves the Grignard reagent by the process of solvation.



Grignard reagent cannot be isolated, therefore, its ethereal solution is directly used in the synthetic reactions. The ease of formation of Grignard reagent depends upon *the nature of both alky or aryl group and the nature* of halogen group. Increasing size of the alkyl group makes the formation of Grignard reagent difficult. For the same alkyl group, the ease of formation follows the order for halogens as $I > Br > C\ell$. Alkyl or aryl magnesium fluorides are not known. Alkyl bromides are the most suitable for preparation of Grignard reagents because alkyliodides are expensive.

17.2.2 Reactivity of Grignard Reagents:

The carbon magnesium bond of Grignard reagent is polar in nature. This is due to higher electronegativity of carbon than magnesium. So the electronic density is lying close to carbon than magnesium. As a result of this electronegativity difference, the carbon atom has a partial negative while magnesium has a partial positive charge.

$$R^{-\delta}-Mg^{+\delta}X$$

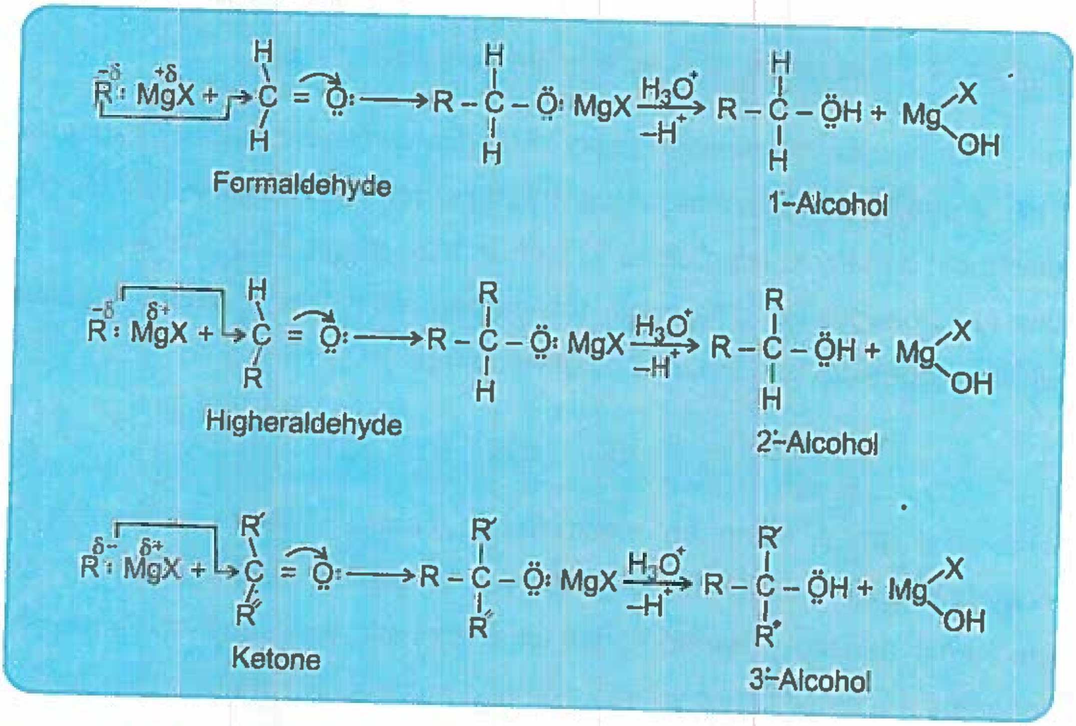
The alkyl group being an electron rich centre, acts as carbanion or nucleophile. It would attack polarized molecules at the point of low electronic density. Therefore, the characteristic reactions of Grignard's reagents are nucleophilic substitution and nucleophilic addition reactions.

17.2.3 Reactions of Grignard Reagents:

Grignard reagents are highly reactive compounds. Therefore, they react with many organic and inorganic compounds to produce a large number of valuable products. Some of these reactions are as follows.

17.2.3.1 Reactions With Aldehydes and Ketones:

Grignard reagents react with aldehydes and ketones to yield addition products. Addition products upon their acid hydrolysis yield alcohols. Formaldehydes produce primary alcohol, higher aldehydes produce secondary, while ketones produce tertiary alcohols on treatment with Grignard reagents.

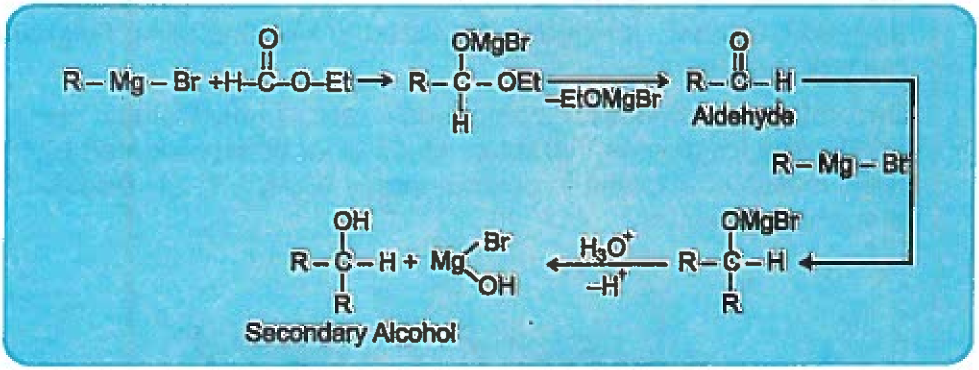


17.2.3.2 Reactions with Esters:

Grignard reagents react with esters to yield carbonyl compounds. These carbonyl compounds react with more of the Grignard reagent in the same reaction mixture and yield alcohols as the final products.

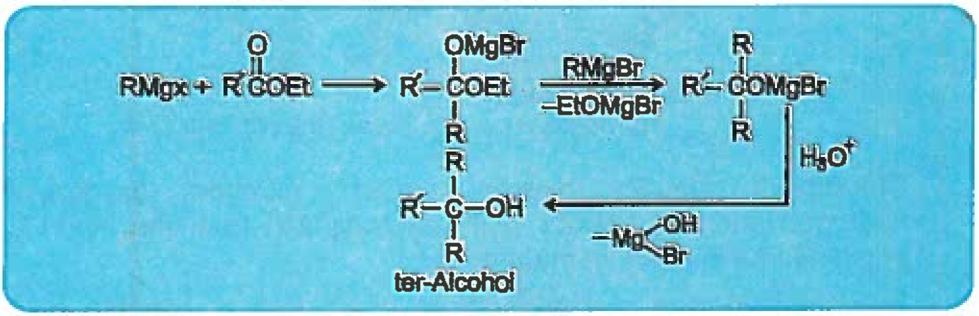
a. Reaction With Ethyl formate:

Ethyl formate reacts with Grignard reagent yielding an addition product. Addition product undergoes elimination and forms aldehyde. This aldehyde further reacts with another molecule of the Grignard reagent and yields secondary alcohol.



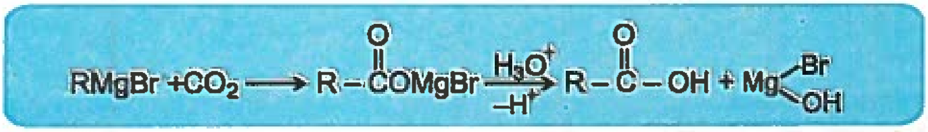
b. Reaction With Ethyl acetate:

Ethyl acetate reacts in the same way as ethyl formate but the end product of this reaction is a tertiary alcohol.



17.2.3.3 Reaction With CO_2:

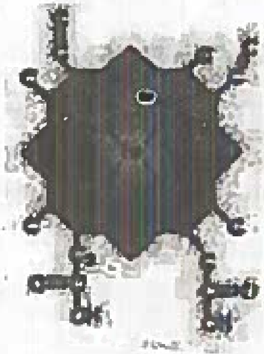
Grignard reagents react with CO_2 forming an addition product. Addition product undergoes acid hydrolysis and yields carboxylic acids.



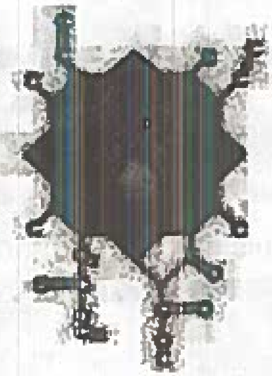
Society, Technology and Science

Alkylhalides are precursors for many organic compounds such as as teflon, alcohol, phenobareton (used in sleeping pills), Grignard reagent, Amines etc.

Several organometallic compounds are under study as candidates for diverse therapies. Much work as investigated by the success of cisplatin in chemotherapy $(C_2H_5)_2$ Ti Cl_2 display anticancer activities.



Human Blood Hemoglobin



Plant Chlorophyll

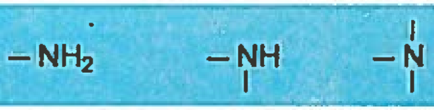
Chlorophyll contains oxygen, carbon, nitrogen, oxygen, hydrogen and magnesium while haemoglobin from the blood contains iron in place of magnesium.

Heamoglobin is a red pigment in blood that is capable of transporting oxygen.

Chlorophyll is the green pigment in plants and certain organism that is capable of trapping energy from the sun to enhance the process of photosynthesis.

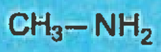
17.3 Amines:

Amines are important nitrogen containing organic compounds. These are the derivatives of NH_3 in which one or more hydrogen atoms have been replaced by one or more similar or different alkyl groups. The functional group of amines may be



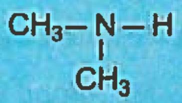
$$-NH_2 \qquad \underset{|}{-NH} \qquad \overset{|}{\underset{|}{-N}}$$

On the basis of the number of alkyl groups directly bonded to nitrogen atom, amines have been classified into primary, secondary and tertiary amines.



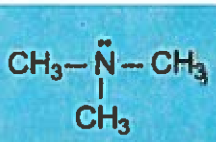
CH_3-NH_2

Primary Amine



$$CH_3-\underset{\underset{CH_3}{|}}{N}-H$$

Secondary Amine



$$CH_3-\underset{\underset{CH_3}{|}}{\ddot{N}}-CH_3$$

Tertiary Amine

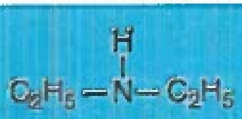
17.3.1 Nomenclature of Amines:

- Primary amines are named by naming the alkyl group attached to nitrogen first followed by the word amine. Names are written as one word.

$CH_3-CH_2-CH_2-NH_2$

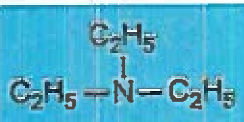
propylamine

- In case of secondary and tertiary amines when two or three identical alkyl groups are attached to nitrogen the prefix “di” and “tri” are added to the name of amine.



$C_2H_5-\overset{\overset{H}{|}}{N}-C_2H_5$

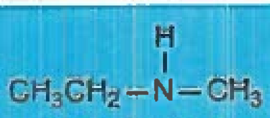
diethylamine



$C_2H_5-\overset{\overset{C_2H_5}{|}}{N}-C_2H_5$

triethylamine

- If different alkyl groups are attached to the nitrogen, then they are named separately in alphabetical order.



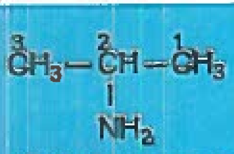
$CH_3CH_2-\overset{\overset{H}{|}}{N}-CH_3$

ethylmethylamine

- In case of complicated amines, IUPAC system is used for naming. According to this system, the amino group is considered as substituent in the chain is represented by the lowest possible number of that carbon atom to which $-NH_2$ group is attached.

CH_3-NH_2

Aminomethane

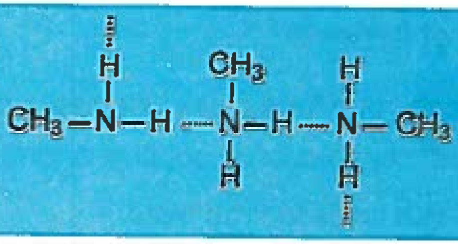


$\overset{3}{C}H_3-\underset{\underset{NH_2}{|}}{\overset{2}{C}H}-\overset{1}{C}H_3$

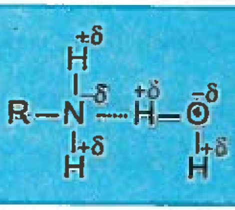
2-Aminopropane

17.3.2 Physical Properties of Amines:

Low molecular weight amines are generally gases or low boiling liquids at room temperature. They possess a characteristic ammonia like smell. Amines have higher boiling points than alkanes of similar molecular weight due to the presence of intermolecular hydrogen bondings. The molecules of primary and secondary amines have high boiling points because they are able to form hydrogen bondings among their molecules.

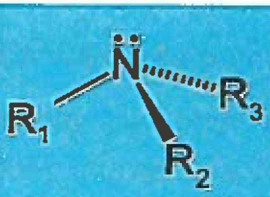


Molecules of tertiary amines cannot form hydrogen bondings among themselves, thus having lower boiling points than primary and secondary amines of the same molecular weight. However, all the primary, secondary and tertiary amines can form hydrogen bondings with water and are soluble in water.



17.3.3 Structure of Amines:

Amines are derivatives of Ammonia (NH_3) molecule where one or more H atoms have been replaced by alkyl groups (R). Since NH_3 molecule has a trigonal pyramidal shape, the resulting amines also have the same geometry. In these amines R–N–H or R–N–R angles is close to tetrahederal angle.



Structure of Amine

17.3.4 Basicity of Amines:

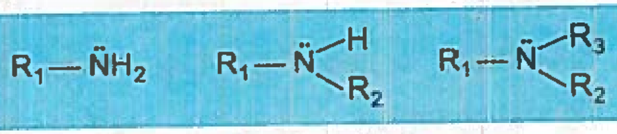
Due to the presence of a lone pair of electrons on the nitrogen atoms $(R-\ddot{N}H_2)$, amines are capable of accepting a proton and are basic in nature. Amines react with acids to form salts.

$$R-\ddot{N}H_2 + HX \xrightarrow[H_2O]{} \underset{\text{amine salt}}{R - \overset{+}{N}H_3\overset{-}{X}}$$

Amines are weak bases and, therefore, partially ionize in aqueous solution with the following equilibrium.

$$R\ddot{N}H_2 + H_2O \rightleftharpoons R\overset{+}{\ddot{N}}H_3 + O\overset{-}{H}$$

Aliphatic amines are stronger bases than NH_3. This is due to the electron –donating alkyl group which increases the electronic density of nitrogen thereby increasing its power of accepting a proton from an acid. The greater the number of alkyl groups, the greater will be the electronic density on nitrogen and, therefore, greater will be the power of nitrogen to accept proton and vice versa.



17.3.5 Preparation of Amines:

Amines can be prepared by a number of different methods. Some of these are given below.

17.3.5.1 Alkylation of Ammonia by Alkyl halides:

When an alkyl halide is heated with alcoholic NH_3, it yields a mixture of primary, secondary, tertiary amines and quaternary ammonium Salt.

During this reaction the hydrogen atoms of NH_3 are replaced by alkyl groups of alkyl halide, therefore, this reaction is also known as alkylation of ammonia.

$$CH_3-Br+NH_3 \longrightarrow CH_3-NH_2+HBr$$

Methylbromide Methylamine

$$CH_3-NH_2+Br-CH_3 \longrightarrow CH_3-NH-CH_3+HBr$$

Dimethylamine

17.3.5.2 Reduction of Nitrogen Containing Functional Groups:

17.3.5.2.1 Reduction of Nitroalkanes:

Primary amines are prepared by the reduction of nitroalkanes with H_2 in the presence of "Pt/Pd" or "Ni" catalyst. They can also be reduced by lithium aluminum hydride in ether.

$$CH_3-NO_2+3H_2 \xrightarrow{Pt/Pd} CH_3-NH_2+2H_2O$$

Nitromethane Methylamine

$$CH_3-CH_2-NO_2+6[H] \xrightarrow[Ether]{LiAlH_4} CH_3-CH_2-NH_2+2H_2O$$

Nitroethane Ethylamine

17.3.5.2.2 Reduction of Nitriles:

When nitriles or alkyl cyanides are reduced they yield the corresponding primary amines. This reduction can be brought about by H_2 in the presence of Ni catalyst or by lithium aluminum hydride in ether.

$$CH_3-C\equiv N+2H_2 \xrightarrow{Ni} CH_3-CH_2-NH_2$$

Methylcyanide Ethylamine

$$CH_3-C\equiv N+4[H]\xrightarrow[\text{Ether}]{\text{LiAlH}_4}CH_3-CH_2-NH_2$$

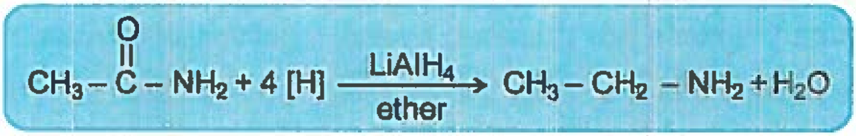
Ethylamine

$$CH_3-CH_2-C\equiv N+4[H]\xrightarrow[\text{Ether}]{\text{LiAlH}_4}CH_3-CH_2-CH_2-NH_2$$

Ethylcynide Propylamine

17.3.5.2.3 Reduction of Amides:

Primary amines are obtained when simple amides are reduced by lithium aluminum hydride in ether.



$$CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-NH_2+4\,[H]\xrightarrow[\text{ether}]{\text{LiAlH}_4}CH_3-CH_2-NH_2+H_2O$$

17.3.6 Reactivity of Amines:

The chemistry of amines is mainly due to the lone pair of electron on nitrogen atom. This lone pair of electrons is available to the electron deficient reagents called electrophiles. On the basis of this lone pair of electrons amines act as nuclcophilic reagents.

17.6.7 Reactions of Amines:

17.6.7.1 Overview

Amines are important and reactive organic compounds. These react with a number of different substances to produce valuable organic compounds. Some of their reactions are:

17.6.7.2 Alkylation of Amines By Alkyl halides:

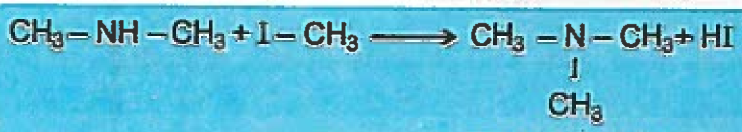
When amines, specially primary amines are treated with alkyl halide, they produce a mixture of secondary, tertiary amines and quaternary ammonium salt. In this process the hydrogen atoms in the amine are successively replaced by the alkyl groups of alkyl halide.

$$R-NH_2+X-R \longrightarrow R-NH-R+HX$$

Primary amine Secondary amine

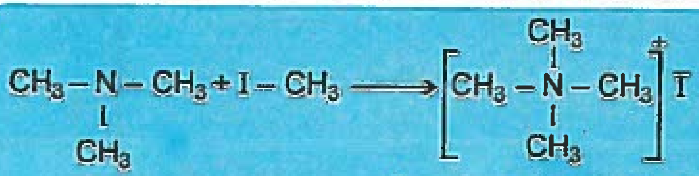
$$CH_3-NH_2+I-CH_3 \longrightarrow CH_3-NH-CH_3+HI$$

Methylamine Dimethylamine



$$CH_3-NH-CH_3+I-CH_3 \longrightarrow CH_3-\underset{\underset{CH_3}{|}}{N}-CH_3+HI$$

Trimethyl amine

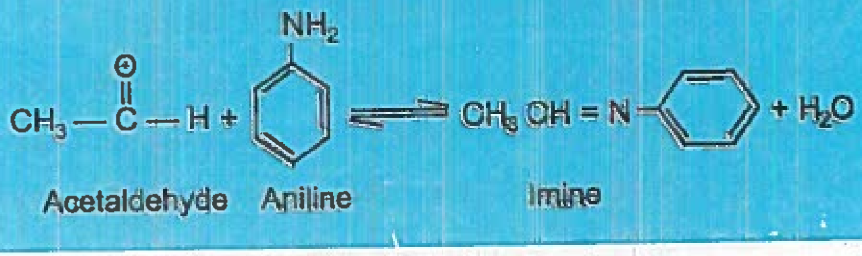


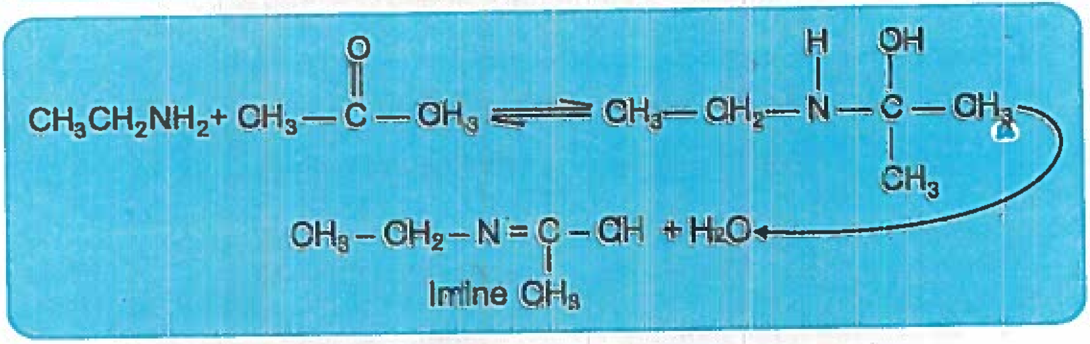
$$CH_3-\underset{\underset{CH_3}{|}}{N}-CH_3+I-CH_3 \longrightarrow \left[CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{N}}-CH_3\right]^{+}\overline{I}$$

Quartenary methyl ammonium iodide

17.6.7.3 Reaction of Amines with Aldehydes and Ketones:

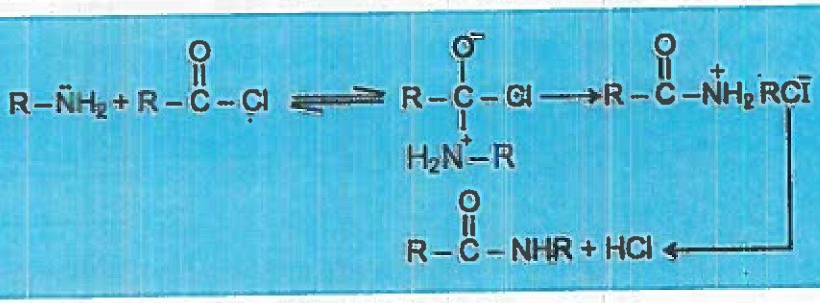
Primary amines react with aldehydes and ketones yielding condensation products called imines. These imines are also known as schiff's bases.





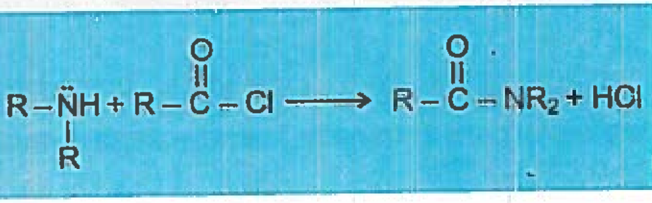
17.6.7.4 Preparation of Amides:

Primary amines react with acid chloride or acid anhydride to produce N – substituted amides.



$$R-\ddot{N}H_2 + R-\overset{O}{\overset{\|}{C}}-Cl \rightleftharpoons R-\underset{H_2\overset{+}{N}-R}{\underset{|}{\overset{O^-}{\overset{|}{C}}}}-Cl \longrightarrow R-\overset{O}{\overset{\|}{C}}-\overset{+}{N}H_2R\bar{Cl} \longrightarrow R-\overset{O}{\overset{\|}{C}}-NHR + HCl$$

Secondary amines react with acid chlorides to produce N, N –disubtituted amides.



$$R-\underset{R}{\underset{|}{\ddot{N}H}} + R-\overset{O}{\overset{\|}{C}}-Cl \longrightarrow R-\overset{O}{\overset{\|}{C}}-NR_2 + HCl$$

As tertiary amines have no hydrogen atom directly attached to the nitrogen, therefore, they don't react with acid chlorides to produce amides.

17.6.7.5 Preparation of Diazonium Salts:

When primary aliphatic amines are treated with nitrous acid they yield highly unstable salts known as diazonium salts. This reaction is termed as diazotization reaction. Nitrous acid being an unstable acid is prepared in situ by the reaction of $NaNO_2$ and dil HCl.

$$CH_3-CH_2-CH_2-NH_2+NaNO_2+2HCl \rightarrow \underbrace{\left[CH_3-CH_2-CH_2-N^+\equiv N\right]\overline{Cl}}_{\text{Diazonium salt}}+2H_2O+NaCl$$

Diazonium salt prepared from aliphatic amines are less important synthetically however the process could be useful analytically. Diazonium salts of aromatic primary amines are of considerable synthetic importance because they serve as intermediates in a variety of synthetic organic reactions, in which the diazonium group $-\overset{+}{N}\equiv N$, is replaced as N_2 by various other functional groups. Aryl bromides, Arylchlorides phenol, Aryl cyanide, benzene are best prepared from diazonium salts.

Key Points:

- General formula of alkyl halide is R–X.
- Each carbon atom in alkyl halide is sp^3 hybridized.
- The molecule which undergoes substitution reaction is called 'substrate'.
- The group or species which leaves the substrate is called "leaving group".
- The end product of substitution is known as reaction product.
- SN^1 Mechanism is defined as that nucleophilic substitution reaction in which only one molecule is involved in rate determing or slow step.
- Those nucleophilic substitution reactions where two species are involved in the rate determing or slow step.
- The primary alkyl halides undergo SN^2 mechanism while tertiary alkyl halides undergo SN^1 Mechanism.
- In polar solvent secondary alkylhalides follow SN^1-mechanism while in non-polar solvents follow SN^2-mechanism.
- During elimination reaction two strong sigma bonds are broken and a new weaker pi bond is formed.
- E^1 stands for unimolecular elimination while E^2 stands for bimolecular elimination reaction.
- Those organic compound which contain at least one carbon—metal bond in their structure are known as organo–metallic compounds.
- Amines are derivatives of NH_3 in which one or more hydrogen atom have been replaced by one or more similar or different alkyl group.
- The functional group of amines may be $-NH_2$, $-\underset{|}{N}H$, or $-\overset{|}{\underset{|}{N}}$
- Due to presence of lone pair of electrons on nitrogen atoms ($R-NH_2$) amines are basic in nature.

Exercise

Q1. Choose the correct option.

1. The reaction of CH_3MgI with acetone followed by hydrolysis gives.
   (a) ter-butanol (b) sec-butanol
   (c) n-butanol (d) none of these
2. Which one of the following halide is most reactive towards nucleophilic substitution reaction?
   (a) C_2H_5Br (b) C_2H_5I
   (c) C_2H_5F (d) C_2H_5Cl
3. All electron deficient species are classified as.
   (a) Nucleophiles (b) Electrophiles
   (c) Bases (d) All of these
4. $R\text{–}CH_2\text{–}X$ is an example of
   (a) Primary alkyl halide (b) Secondary alkyl halide
   (c) Isopropyl halide (d) Both (a) and (b)
5. The carbon atom carrying positive charge and attached to three other atoms or groups is called.
   (a) Carbonium ion (b) Carbon ion
   (c) Oxonium ion (d) Carbanion
6. Grignard reagent can be represented by general formula
   (a) R–Mg– N (b) R–Mg–O
   (c) R–Mg–OH (d) R–Mg–X

7. The end product of reaction of Grignard reagent with Ethyl acetate is

(a)	primary alcohol	(b)	secondary alcohol
(c)	tertiary alcohol	(d)	none of these

8. An electron pair donor is classified as

(a)	Lewis acid	(b)	Lewis base
(c)	Bronsted acid	(d)	Bronsted base

9. In primary alkyl halides the carbon atom to which the halo group is attached is in turn bonded directly to

(a)	one other carbon	(b)	two other carbons
(c)	three other carbons	(d)	four other carbons

Q II Short questions.

1. What is the importance of Grignard reagent?
2. Compare nucleophilic substitution reaction and electrophilic substitution reaction.
3. Why tertiary carbocation is more stable?
4. In reaction between chloroethane and aqueous sodium hydroxide identify the attacking nucleophile and atom in the chloro-ethane molecule being attacked.
5. What is the importance of diazonium salt?
6. Define the following terms.

(a)	substrates	(b)	leaving group
(c)	carbocation		

QIII. Long questions

1. Discuss various methods of preparation of alkyl halides.
2. Explain elimination reaction in alkyl halides.
3. Discuss the mechanism of SN^1 and SN^2 reactions.
4. (a) How can you prepare Grignard reagent.
   (b) Discuss the reaction of Grignard reagent with.
   (i) aldehydes (ii) ketones
   (iii) esters (iv) carbon dioxide
5. How amines are prepared? Discuss its structure and acidity.
6. Write down different reactions of amines.