Chapter
17

Alkyl Halides and Amines

Major Concepts

17.1 Alkyl Halides
17.2 Organometallic Compounds (Grignard's Reagents)
17.3 Amines

Learning Outcomes:

Students will be able to:

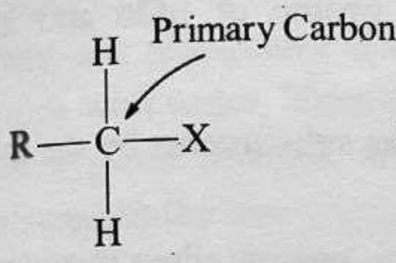
- Name alkyl halides using IUPAC system. **(Applying)**
- Discuss the structure and reactivity of RX. **(Applying)**
- Describe the preparation of RX by the reaction of alcohols with HX, $SOCl_2$ and PX_3 and by radical halogenation of alkanes. **(Applying)**
- Describe the mechanism and types of nucleophilicsubstitution reactions. **(Understanding)**
- Describe the mechanism and types of elimination reactions. **(Understanding)**
- Describe the preparation and reactivity of Grignard's Reagents. **(Applying)**
- Discuss chemistry of Grignard's reagent by the addition of aldehydes, ketones, esters and carbon dioxide. **(Understanding)**
- Discuss nomenclature, structure and basicity of amines. **(Applying)**
- Describe the preparation of amines by alkylation of ammonia to RX and reduction of nitriles, nitro and amide functional groups. **(Applying)**
- Discuss reactivity of amines. **(Applying)**
- Describe chemistry of amines by alkylation of amines with RX, reactions with aldehydes, ketones, preparation of amides and diazonium salts. **(Understanding)**
- Describe isomerism in alkyl halides and amines. **(Understanding)**

Introduction

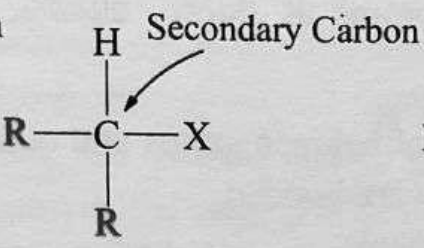
Alkyl halides are one of the most important types of reactants in nucleophilic substitution reactions. In this chapter, we consider the properties and reactions of alkyl halides and then study the two of the most important types of reactions in organic chemistry, namely the substitution and elimination reactions. In this chapter, we also discuss the basicity and properties of amines.

17.1 Alkyl Halides

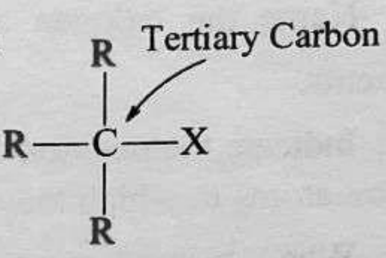
Alkyl halides are organic compounds containing a halogen atom covalently bonded to one of the saturated carbon atoms of an alkyl group. They are termed as, in the IUPAC system of nomenclature, haloalkanes. They are classified as primary (1°), secondary (2°) or tertiary (3°) alkyl halides depending upon whether the halogen atom is directly bonded to primary, secondary or tertiary carbon atom.



Primary Alkyl Halide



Secondary Alkyl Halide



Tertiary Alkyl Halide

Their general formula is $C_nH_{2n+1}X$, where X = F, Cl, Br, or I.

17.1.1 Nomenclature of Alkyl Halides

There are two systems for naming alkyl halides that is common system and IUPAC system.

17.1.1.1 Common System

The common names of alkyl halides are two word names. Common names are constructed by naming the alkyl group first and then the halide as fluoride, chloride, bromide and iodide. These names are useful only for simple alkyl halides. Examples are:

CCl_4

Carbon **tetrachloride**

$CHCl_3$

Chloroform

CH_2Cl_2

Methylene **chloride**

CH_3-Cl

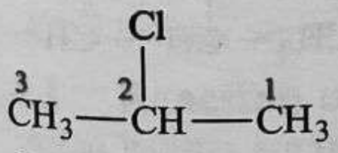
Methyl **chloride**

$\overset{2}{C}H_3-\overset{1}{C}H_2-F$

Ethyl **fluoride**

$\overset{3}{C}H_3-\overset{2}{C}H_2-\overset{1}{C}H_2-I$

n-Propyl **iodide**



$\overset{3}{C}H_3-\overset{2}{\underset{}{C}}H(Cl)-\overset{1}{C}H_3$

Isopropyl **chloride**

$(CH_3)_3CBr$

Tert.butyl **bromide**

17.1.1.2 IUPAC System

In this system, alkyl halides are considered as halogen derivatives of corresponding alkane and are named as ***haloalkanes***. The IUPAC names of alkyl halides are one-word names. The rules for naming alkyl halides are:

Step 1: Select the longest continuous chain of carbon atoms containing the halogen atom.

Step 2: Number the carbon chain from that end which is nearer to halogen atom.

Step 3: Name the halogen atoms as fluoro, chloro, bromo or iodo and all other substituents.

Step 4: Indicate the position of halogen atoms and other substituents by the number of carbon atoms to which they are bonded.

Step 5: When two or more different substituents are present, then they are named alphabetically.

Examples are:

CH_3-Cl

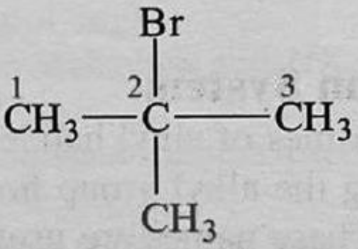
Chloromethane

CH_3-CH_2-F

Fluoroethane

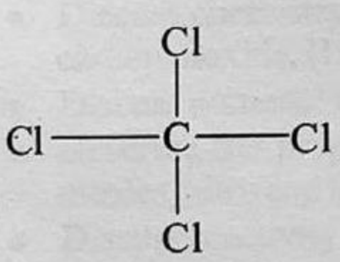
$\overset{3}{C}H_3-\overset{2}{C}H_2-\overset{1}{C}H_2-I$

1-Iodopropane



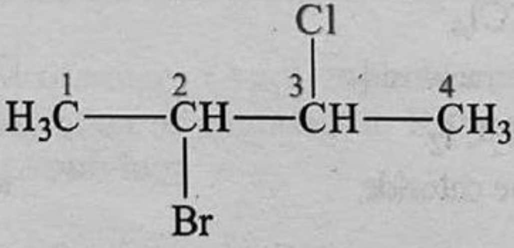
$$\overset{1}{C}H_3-\underset{\underset{\displaystyle CH_3}{|}}{\overset{\overset{\displaystyle Br}{|}}{\overset{2}{C}}}-\overset{3}{C}H_3$$

2-Bromo-2-methylpropane



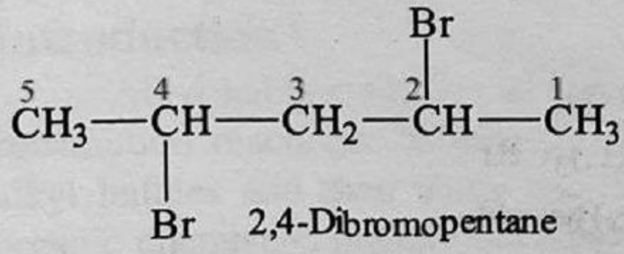
$$Cl-\underset{\underset{\displaystyle Cl}{|}}{\overset{\overset{\displaystyle Cl}{|}}{C}}-Cl$$

Tetrachloromethane



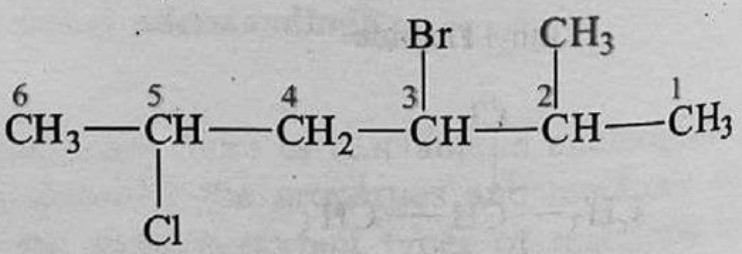
$$H_3\overset{1}{C}-\underset{\underset{\displaystyle Br}{|}}{\overset{2}{C}H}-\overset{\overset{\displaystyle Cl}{|}}{\overset{3}{C}H}-\overset{4}{C}H_3$$

2-Bromo-3-chlorobutane



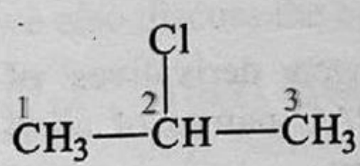
$$\overset{5}{C}H_3-\underset{\underset{\displaystyle Br}{|}}{\overset{4}{C}H}-\overset{3}{C}H_2-\overset{\overset{\displaystyle Br}{|}}{\overset{2}{C}H}-\overset{1}{C}H_3$$

2,4-Dibromopentane



$$\overset{6}{C}H_3-\underset{\underset{\displaystyle Cl}{|}}{\overset{5}{C}H}-\overset{4}{C}H_2-\overset{\overset{\displaystyle Br}{|}}{\overset{3}{C}H}-\overset{\overset{\displaystyle CH_3}{|}}{\overset{2}{C}H}-\overset{1}{C}H_3$$

3-Bromo-5-chloro-2-methylhexane



$$\overset{1}{C}H_3-\overset{\overset{\displaystyle Cl}{|}}{\overset{2}{C}H}-\overset{3}{C}H_3$$

2-Chloropropane

17.1.2 Physical Properties of Alkyl Halides

i) Lower alkyl halides such as CH_3Cl, CH_3Br, CH_3F and CH_3CH_2Cl are gases at room temperature. The alkyl halides up to C_{18} are colourless liquids and those further than C_{18} are colourless solids.

ii) They are practically insoluble in water because they do not form hydrogen bonds with water. They are readily soluble in organic solvents.

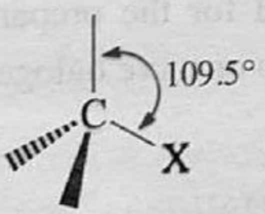
iii) For a given halogen atom, the boiling points of alkyl halides increase with increase in the size (or mass) of the alkyl group.

iv) For a given alkyl group, the boiling points of alkyl halides are in the order: **RI >** RBr > RCl > RF

v) For a given halogen atom, the density of alkyl halides decrease with increase in the size (or mass) of the alkyl group.

17.1.3 Structure of Alkyl Halides

Let us consider the example of simple alkyl halide (i.e. methyl chloride). The carbon atom to which the halogen is bonded is sp^3 hybridized. The halogen (chlorine) atom has one half-filled p orbital. The carbon-halogen σ-bond is formed by head to head overlap of one sp^3 hybrid orbital of carbon and one half-filled p orbital of halogen atom. The carbon-hydrogen σ-bond is formed by head to head overlap of one sp^3 hybrid orbital of carbon and half-filled s orbital of hydrogen atom.



The $H\hat{C}H$ and $H\widehat{C}X$ bond angles are nearly 109.5°. The arrangement of atoms or groups around the carbon atom is usually tetrahedral.

17.1.4 Preparation of Alkyl Halides

Alkyl halides are prepared by the methods given below:

17.1.4.1 Reaction of Alcohols with Hydrogen Halides

Alkyl halides are prepared by the reaction of alcohol with hydrogen halides in the presence of dehydrating agent such as anhydrous $ZnCl_2$.

$$CH_3CH_2OH + HCl \xrightarrow{ZnCl_2} CH_3CH_2Cl + H_2O$$

The order of reactivity of hydrogen halides is: HI > HBr > HCl

The order of reactivity of alcohols is: 3° > 2° > 1°

17.1.4.2 Reaction of Alcohols with other Halogenating Agent ($SOCl_2$, PX_3)

Reaction of Alcohols with Thionyl Halides

Alkyl halides are prepared by heating alcohols with thionyl halides in the presence of pyridine.

$$CH_3CH_2OH + SOCl_2 \xrightarrow{\text{Pyridine}} CH_3CH_2Cl + SO_2 + HCl$$

This is the best method for the preparation of alkyl halides because both the products (SO_2 and HCl) are in gaseous state and can be removed easily.

Reaction of Alcohols with Phosphorus Halides (PX_3)

Alkyl halides are prepared by the reaction of alcohols with phosphorous halides.

$$3\,CH_3CH_2OH + PCl_3 \longrightarrow 3\,CH_3CH_2Cl + H_3PO_3$$

17.1.4.3 Radical Halogenation of Alkanes

Alkyl halides are prepared by the reaction of alkanes with halogens in the presence of diffused sun light or UV light.

$$CH_3CH_3 + Cl_2 \xrightarrow{\text{UV Light}} CH_3CH_2Cl + HCl$$

This is not a good method for the preparation of alkyl halides because the halogen derivatives containing two or more halogen atoms are also formed along with alkyl halides.

17.1.5 Reactivity of Alkyl Halides

Alkyl halides are very reactive compounds. The extent of reactivity depends upon two factors: (i) bond polarity of carbon-halogen bond (ii) bond energy of carbon-halogen bond.

17.1.5.1 Bond Polarity of Carbon-Halogen Bond

The halogen atom in alkyl halides is more electronegative than carbon. Because of this, the molecule of alkyl halide is polarized due to the greater electronegativity of halogens as compared to carbon. Greater the electronegativity difference (ΔEN) of carbon and halogen atoms, greater would be the polarity of C—X bond. Greater the polarity, greater would be the bond strength and lesser would be the reactivity of RX.

Table 17.1: Dipole Moment of Halomethanes

Halomethane	Electronegativity of Halogen	EN Difference between C and X	Dipole moment (in Debye unit)
CH_3F	3.98	3.98−2.50 = 1.48	1.85
CH_3Cl	3.00	3.00−2.50 = 0.50	1.87
CH_3Br	2.96	2.96−2.50 = 0.46	1.81
CH_3I	2.56	2.56−2.50 = 0.06	1.62

17.1.5.2 Bond Energy of Carbon-Halogen Bond

Bond energy is the measure of bond strength. Greater the bond energy, greater would be the bond strength and lesser would be the reactivity of C—X bond.

Table 17.2: Bond Energy of C—X Bonds

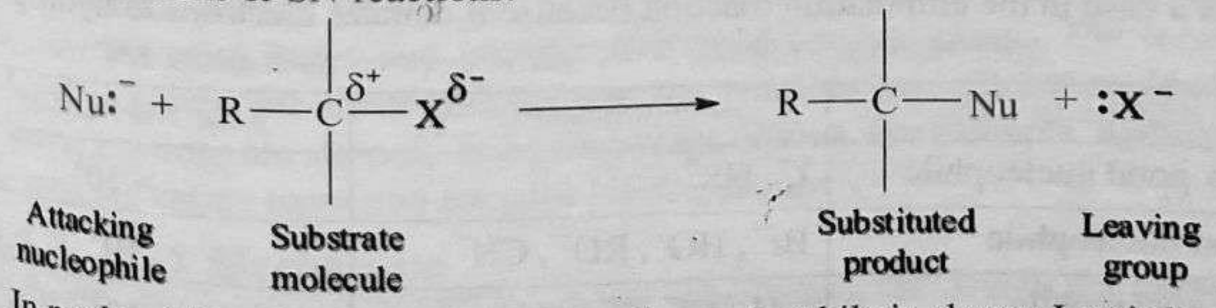
Bond	Bond Energy (kJ/mol)
C—F	467
C—Cl	346
C—Br	290
C—I	228

The order of reactivity of alkyl halides is: RI > RBr > RCl > RF

17.1.6 Nucleophilic Substitution Reactions

17.1.6.1 General Introduction

The reactions in which an electron rich nucleophile replaces another nucleophile (leaving group) to form a new molecule are called nucleophilic substitution reactions or SN-reactions.



$$Nu:^- + R-\overset{\delta^+}{C}-X^{\delta^-} \longrightarrow R-C-Nu + :X^-$$

In nucleophilic substitution reactions, the nucleophile is always Lewis base and it may be neutral or negatively charged. The substrate is frequently an alkyl halide and the leaving group is a halide ion. The partial positive carbon atom of alkyl halides acts as an electrophile and has ability to accept a pair of electrons from attacking nucleophile. In this way, a new bond is formed between the nucleophile and carbon of alkyl halide.

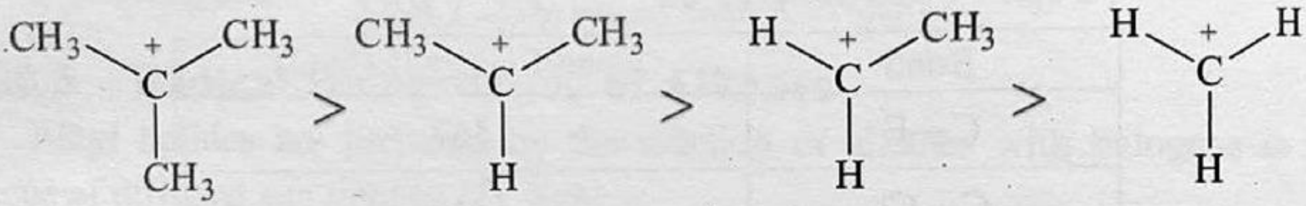
The S_N reactions occur by S_N1 mechanism or by S_N2 mechanism.

17.1.6.2 Important Concepts

Carbocations and Their Stability

Carbocations are very reactive unstable electron deficient species. Anything which donates electron density to the electron deficient centre will help to stabilize them.

Alkyl groups are weak electron donating groups and thus stabilize nearby carbocations. In general, more substituted carbocations are more stable. This means that tertiary carbocations are more stable than secondary which in turn are more stable than primary. In other words, tertiary carbocations are the most stable and the methyl carbocation is the least stable. The overall order of stability is given below:



Tertiary carbocation
Secondary carbocation
Primary carbocation
Methyl carbocation

Nucleophile and Base

Both nucleophiles and Lewis bases are electron pair donor species. Then what is the difference between a nucleophile and a base?

Base is a specie that donates an electron pair to hydrogen (a proton) and nucleophile is a specie that donates an electron pair to an atom other than hydrogen particularly carbon atom. A nucleophile can also be called a base when this donation happens towards a hydrogen ion (a proton). For example, the hydroxide ion acts as a nucleophile in the substitution reaction because it donates electrons to carbon but it acts as a base in the elimination reaction because it donates electrons to hydrogen.

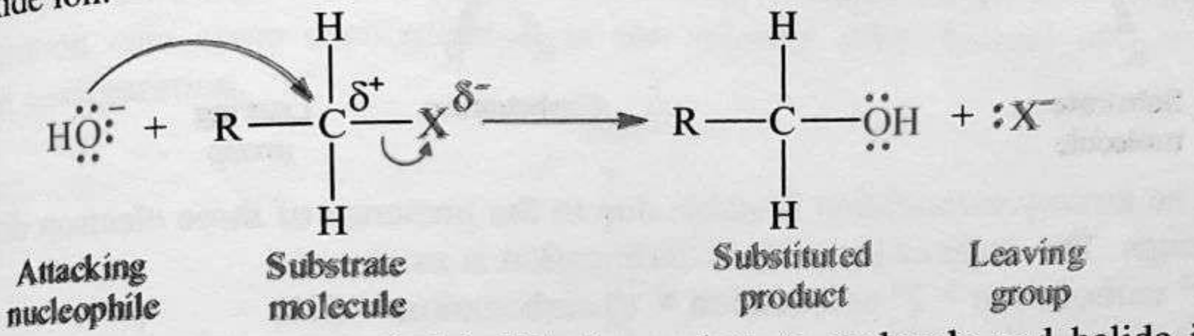
Table 17.3: Some Common Nucleophiles and their Nucleophilicity

Reactivity Class	Nucleophile	Relative Reactivity
Very good nucleophile	I^-, HS^-	$> 10^5$
Good nucleophile	Br^-, HO^-, RO^-, CN^-	10^4
Fair nucleophile	NH_3, Cl^-, F^-	10^3
Weak nucleophile	H_2O, ROH	10^0
Very weak nucleophile	RCOOH	10^{-2}

Substrate and Leaving Group

The substrate may be defined as: the carbon containing compound on which substitution takes place. It is the reactant to which the nucleophile became bonded and from which the leaving groups departed.

The leaving groups may be defined as: the species that depart from substrate and take a pair of electrons with them. Consider the reaction of alkyl halide with hydroxide ion.



In this reaction, the alkyl halide is a substrate molecule and halide ion is a leaving group. The bond between carbon and leaving group is polar because the leaving group is more electronegative than carbon. The leaving group has partial negative charge and the carbon has partial positive charge. Thus the carbon acts as an electrophile and is reactive towards nucleophile.

Table 17.4: Some Common Leaving Groups

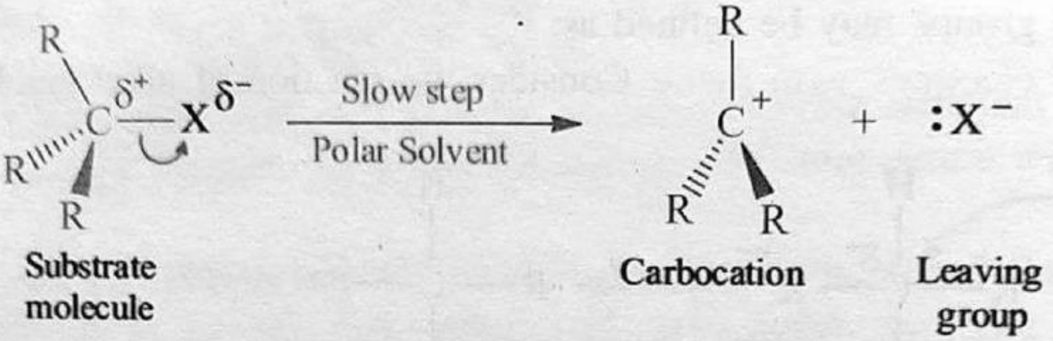
Class	Leaving Group
Good leaving groups	I^-, Br^-, Cl^-, H_2O
Moderate leaving groups	HS^-, CN^-, NH_3
Poor leaving groups	F^-, HO^-, RO^-
Very poor leaving groups	NH_2^-, H^-, R^-

The best leaving groups are those that become the most stable ions after they depart. The best leaving groups are weakly basic molecules or ions. For example, halide ions are weak bases and are therefore good leaving groups. Conversely, the poor leaving groups are those that become the unstable ions after they depart. The poor leaving groups are strongly basic molecules or ions. For example, hydroxide and amide ions are strong bases and are poor leaving groups.

17.1.6.3 S_N1 Mechanism

In the designation S_N1, "S" stands for *substitution*, "N" stands for *nucleophilic* and "1" stands for *unimolecular*. Unimolecular means that only one molecule is involved in the rate-determining step. In this mechanism, the breaking of bond between carbon and the leaving group is fully completed before bond making with the nucleophile starts. Consider the reaction of *tertiary* alkyl halide with nucleophile. The reaction occurs in two steps.

Step 1: The *tert*-alkyl halide ionizes to produce a planar carbocation and a leaving group.

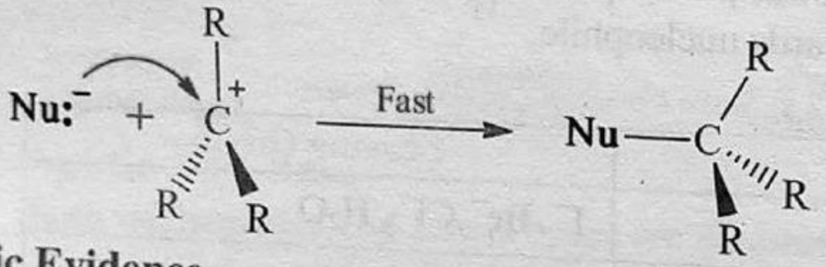


The tertiary carbocation is stable due to the presence of three electron donating alkyl groups. The order of stability of carbocation is as:

3° carbocation > 2° carbocation > 1° carbocation > CH_3^+

This step of reaction is the rate determining step. Since this step involves the breakage of covalent bond so it is a slow step.

Step 2: The nucleophile attacks the planar carbocation to produce *tert.*alkyl product. Since the second step involves the combination of cations and anions, so it is fast.



Kinetic Evidence

The rate law for the reaction is:

Rate ∝ $[R_3CX]$

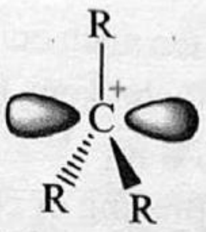
Rate = $k[R_3CX]$

Where **'k'** is the rate constant.

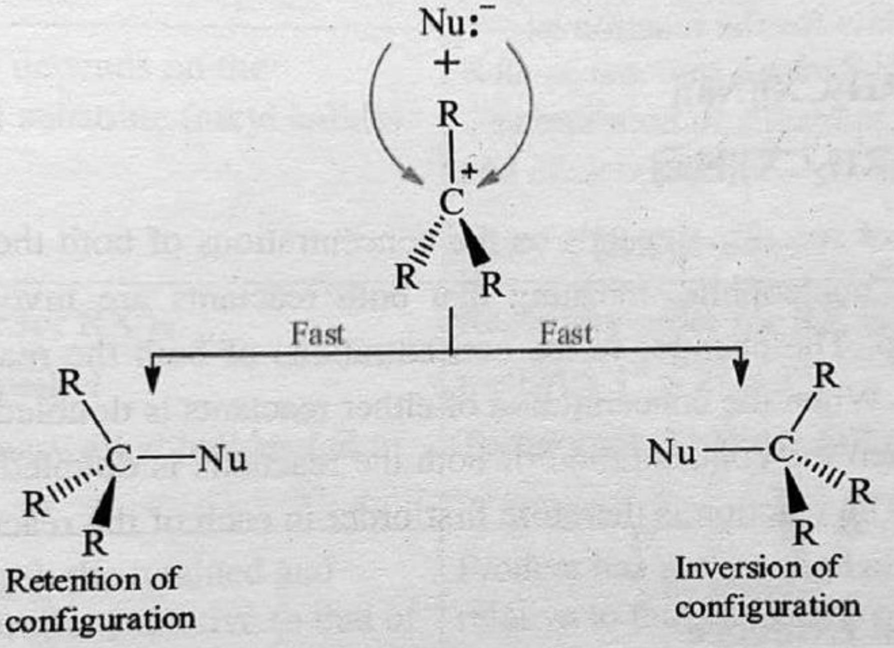
The rate of reaction depends only on the concentration of the substrate, *tert.*alkyl halide but it does not depend on the concentration of the nucleophile. Doubling the concentration of the *tert.*alkyl halide doubles the rate of the reaction, but changing the concentration of the nucleophile has no effect on its rate. This rate equation is first order overall.

Stereochemical Evidence

Positively charged carbon of carbocation intermediate is sp^2 hybridized and has one pure *p* orbital with two lobes. The three substituent's bonded to positively charged carbon are in the same plane. The empty unhybridized *p*- orbital on carbon perpendicular to the plane of molecule with one lobe on each side of the plane.



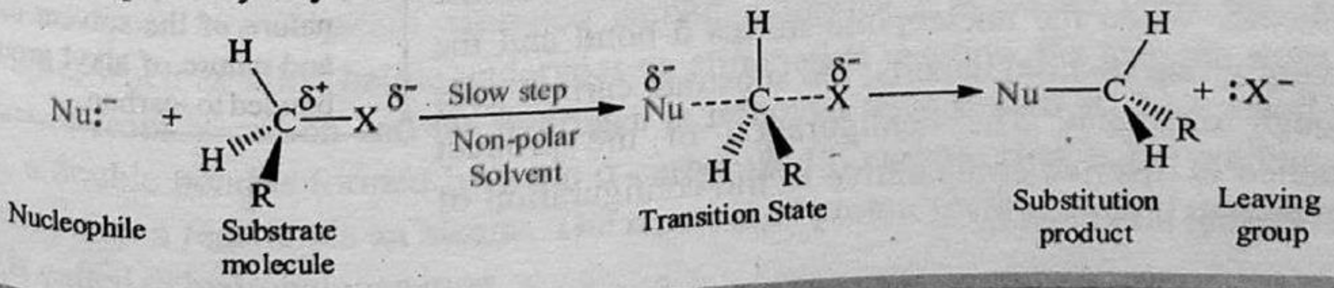
In the second step of the S_N1 mechanism, the nucleophile can attack the carbocation from either side of the plane, therefore some of the product has retained configuration (the same configuration as the reacting alkyl halide) and some has inverted configuration.



When complete inversion of configuration is observed in a substitution reaction, we realize that the mechanism is S_N2 but not S_N1.

17.1.6.4 S_N2 Mechanism

In the designation S_N2, "S" stands for *substitution*, "N" stands for *nucleophilic* and "2" stands for *bimolecular*. Bimolecular means that two molecules (both the alkyl halide and nucleophile) are involved in the rate-determining step. In this mechanism, the breaking of bond between carbon and the leaving group as well as the formation of bond between a nucleophile and an electrophile occur simultaneously. Consider the reaction of *primary*alkyl halide with nucleophile. The reaction occurs in one step.



In transition state, the bond to the nucleophile is partially formed, and the bond to the leaving group (halide) is partially broken. The transition state has very short-lived existence.

This is slow step and rate determining or controlling step of reaction. Since two molecules are involved in rate determining step, hence it is called bimolecular reaction.

Kinetic Evidence

The rate law for the reaction is:

$$\mathbf{Rate} \propto [\mathrm{RH_2CX}][\mathrm{Nu}\overset{-}{:}]$$

$$\mathbf{Rate} = k[\mathrm{RH_2CX}][\mathrm{Nu}\overset{-}{:}]$$

The rate of reaction depends on the concentrations of both the substrate (alkyl halide) and the nucleophile, meaning that both reactants are involved in the rate determining step. The changes in the concentrations of both the reactants affect the rate of reaction. When the concentration of either reactants is doubled, the rate should be doubled. When the concentration of both the reactants is doubled, the rate should be quadruples. The reaction is therefore first order in each of the reactants and second orders overall.

Stereochemical Evidence

In primary alkyl halides, the electrophilic carbon is bonded with one alkyl group and two small hydrogen atoms. These two hydrogen atoms do not show steric hindrance due to smaller size and give way to attacking nucleophile to attack on electrophilic carbon from back side of leaving group. The nucleophile cannot attack on electrophilic carbon atom from front side of the leaving group. We may say that the leaving group blocks the approach of the nucleophile to the front side of the molecule. When the nucleophile makes a bond and the leaving group (halide) departs, the substrate carbon goes through inversion. The configuration of the product obtained is inverted comparative to the configuration of the reactant alkyl halide.

Keep in Mind

- **Methyl halide and primary alkyl halides undergo S_N2 reactions only.**
- **Tertiary alkyl halides undergo S_N1 reactions only.**
- **Secondary alkyl halides undergo both S_N1 and S_N2 reactions depending on the nature of the solvent used and nature of alkyl groups bonded to -carbon.**

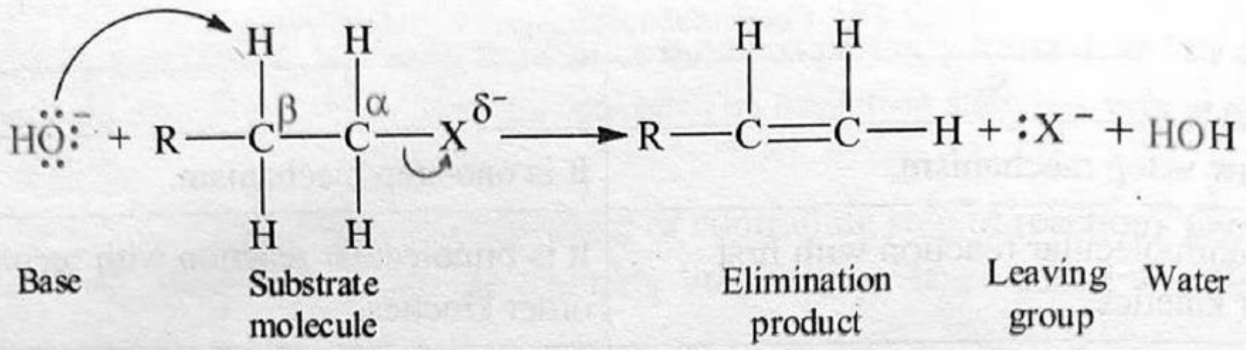
Table 17.5: Comparison of S_N1 and S_N2 Mechanisms

S_N1	S_N2
It is two-step mechanism.	It is one-step mechanism.
It is unimolecular reaction with first order kinetics.	It is bimolecular reaction with second order kinetics.
Reaction proceeds through the formation of carbocation.	Reaction proceeds through the formation of transition state.
Rate of reaction depends on the concentration of substrate (alkyl halide) only. Rate $\propto$ [RX]	Rate of reaction depends on the concentration of substrate (alkyl halide) and nucleophile. Rate $\propto$ [RX][$\bar{Nu:}$]
Reactivity order for RX is: 3° > 2° > 1° > methyl Methyl and primary alkyl halides fail to react.	Reactivity order for RX is: methyl > 1° > 2° > 3° Tertiary alkyl halides fail to react.
Products have both the retained and inverted configurations relative to that of the reactant (alkyl halide).	Product has the inverted configuration relative to that of the reactant (alkyl halide).
It is favoured by polar solvents.	It is favoured by non-polar solvents.
It is favoured by weaker nucleophiles.	It is favoured by stronger nucleophiles.

17.1.7 1,2-Elimination Reactions

17.1.7.1 Overview

In addition to S_N reactions, alkyl halides also undergo elimination reactions. An elimination reaction is a type of organic reaction in which two substituents are removed from two adjacent saturated carbon atoms of a substrate molecule. For example, when an alkyl halide undergoes an elimination reaction, the halogen atom is removed from α-carbon and the hydrogen is removed from β-carbon. As a result of this, a double bond is formed between α-carbon and β-carbon. Hence, the product of an elimination reaction is an alkene. The removal of proton (hydrogen ion) and halide ion is called dehydrohalogenation.

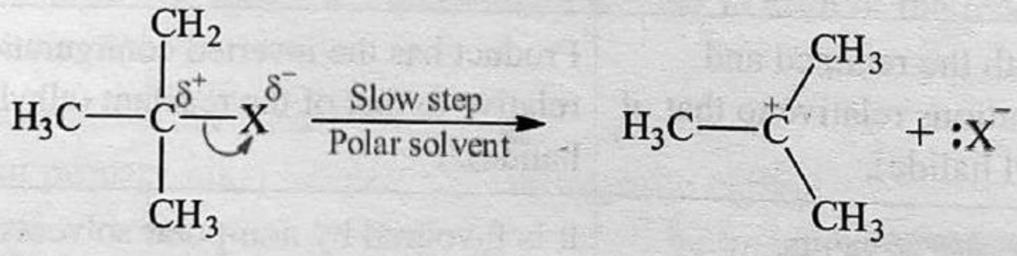


The most common bases used in elimination reactions are HO^-, RO^- and H_2N^-. There are two important mechanisms for elimination reactions viz. E2 and E1 just like for S_N reactions.

17.1.7.2 E1 Mechanism (Unimolecular Elimination)

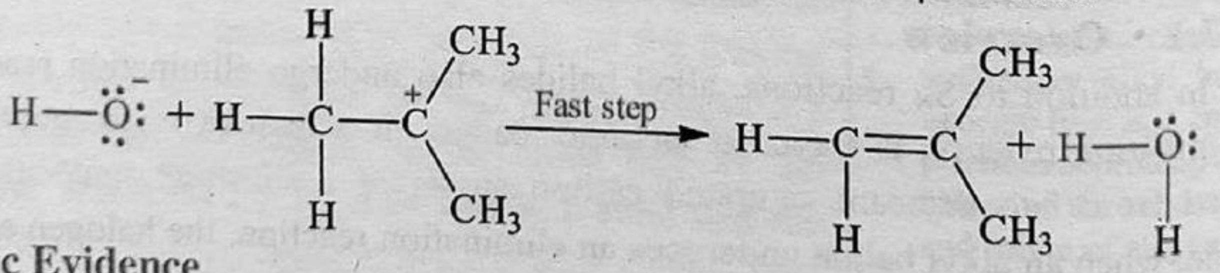
In the designation E1, "E" stands for *elimination* and "1" stands for *unimolecular*. Unimolecular means that only one molecule is involved in the rate-determining step. In this mechanism, the breaking of bond between carbon and the leaving group is fully completed before any reaction occurs with the base to lose a hydrogen. Consider the reaction of *tert*.alkyl halide with base. The reaction occurs in two steps.

Step 1: The *tert*-butyl halide undergoes ionization to produce a planar carbocation and a leaving group. The bond breaks between halogen atom and α-carbon atom.



This step of reaction is the rate determining step. Since this step involves the breakage of covalent bond so it is a slow step.

Step 2: The base (HO^-) removes a proton from one of the β-carbon and with the removal of halide ion, a new π-bond is formed between α and β-carbons.



Kinetic Evidence

The rate law for the reaction is:

$$\text{Rate} \propto [(CH_3)_3CX]$$

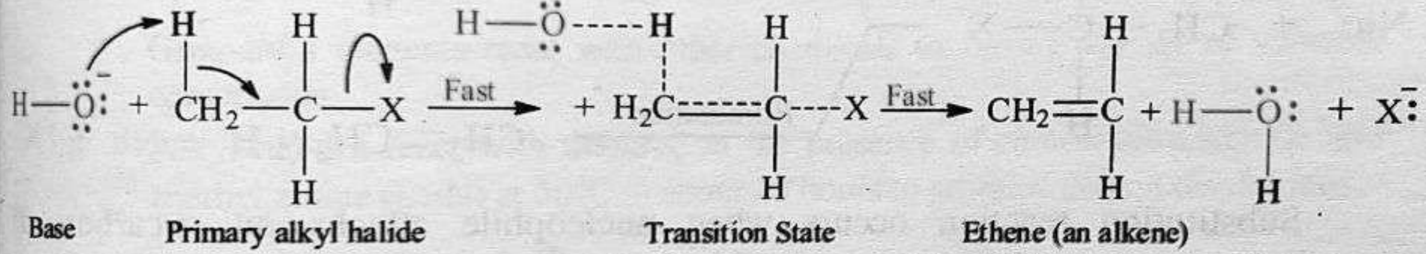
$$\text{Rate} = k[(CH_3)_3CX]$$

Where 'k' is the rate constant.

The rate of reaction depends only on the concentration of the substrate, *tert*-butyl halide but it does not depend on the concentration of the base. This rate equation is first order overall.

17.1.7.3 E2 Mechanism (Bimolecular Elimination)

In the designation E2, "E" stands for *elimination* and "2" stands for *bimolecular*. Bimolecular means that both the alkyl halide and base are involved in the rate-determining step. In this mechanism, the breaking of bond between carbon and the leaving group as well as the reaction with the base to lose a proton (hydrogen) occurs simultaneously. Consider the reaction of *primary* alkyl halide with base. The reaction occurs in one step.



In the transition state, the bond of base to one of the β-hydrogen and the bond between α and β-carbon atoms are partially formed. On the other hand, the bond of β-hydrogen to carbon and the bond between α-carbon and leaving group is partially broken.

This is slow step and rate determining or controlling step of reaction. Since two molecules are involved in rate determining step, hence it is called bimolecular reaction.

Kinetic Evidence

The rate law for the reaction is:

Rate $\propto$ $[RH_2CX][\bar{O}H]$

Rate = $k[RH_2CX][\bar{O}H]$

Where '**k**' is the rate constant.

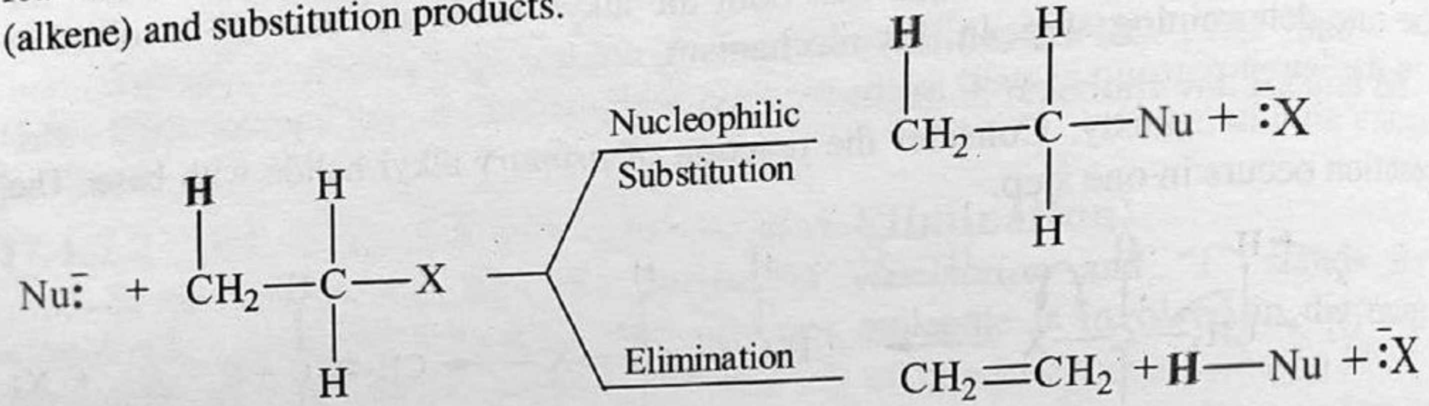
The rate of reaction depends on the concentrations of both the substrate (alkyl halide) and the base. The changes in the concentrations of both the reactants affect the rate of reaction. When the concentration of either reactants is doubled, the rate should be doubled. When the concentration of both the reactants is doubled, the rate should be quadruples. The reaction is therefore second order.

Keep in Mind

- **Primary alkyl halides undergo E2 reactions only.**
- **Secondary and Tertiary alkyl halides undergo both E1 and E2 reactions.**

17.1.8 Substitution versus Elimination

All nucleophiles are possible bases and all bases are possible nucleophiles. Hence, the reactive part of both nucleophiles and bases is an unshared electron pair. Elimination reactions occur simultaneously with substitution reactions. There is always a competition between elimination and substitution reactions. For example, the reaction of nucleophile (base) with an alkyl halide produce mixture of elimination (alkene) and substitution products.



Substitution reaction occurs when nucleophile attacks on α-carbon. If nucleophile attacks on β-hydrogen, elimination reaction occurs. The ratio of products formed depends on the relative rates of the substitution and elimination reactions. The relative rates of elimination and substitution reactions are affected by the following factors:

i) Nature of Solvent

Polar solvents favour substitution reactions while non-polar solvents favour elimination reactions. In aqueous medium (more polar solvent), the main reaction will be substitution and elimination will be a side reaction. In alcoholic medium (less polar solvent), the main reaction will be elimination and substitution will be a side reaction.

ii) Nature of base

Strong bases favour elimination reactions. In the presence of strong base, the main reaction will be elimination and substitution reaction will be a side reaction.

iii) Effect of Temperature

An increase in temperature will favour elimination than substitution.

iv) Nature of Substrate

Crowding within the substrate favours elimination over substitution.

v) Nature of Alkyl Halide

Primary alkyl halides favour mainly substitution reactions while tertiary alkyl halides mainly favour elimination reactions. Secondary alkyl halides favour both substitution and elimination.

Society, Technology and Science

Alkyl Halides as Precursors

A compound that participates in a chemical reaction and produces another compound is called precursor. Alkyl halides are, therefore, act as precursors and produce many other organic chemicals in the lab such as thiols, Grignard reagents and dialkyl disulphides.

i) Alkyl halides react with an excess of KOH and H_2S to produce thiols.

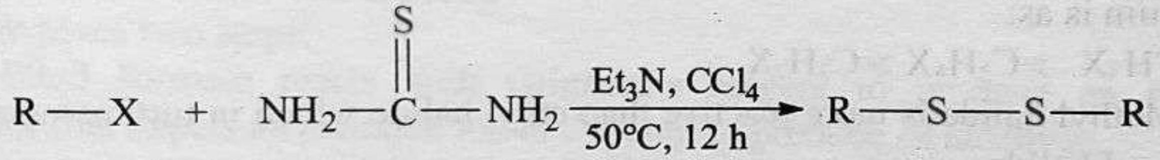
$$R—X + KOH + H_2S \longrightarrow R—SH + H_2O + KX$$

ii) Alkyl halides react with magnesium metal in the presence of pure diethyl ether in the absence of moisture, CO_2, or O_2 to produce Grignard reagents.

$$R—X + Mg \xrightarrow{\text{Ether}} R—Mg—X$$

Grignard's reagents react with other chemicals to form a variety of valuable compounds.

iii) Alkyl halides react with thiourea in the presence of carbon tetrachloride and triethyl amine (Et_3N) at 50°C in about 12 hours to produce dialkyl disulphides.



$$R—X + NH_2—\overset{\overset{\displaystyle S}{\|}}{C}—NH_2 \xrightarrow[50°C,\ 12\ h]{Et_3N,\ CCl_4} R—S—S—R$$

Dialkyl disulphide is used to make other chemicals.

17.2 Organometallic Compounds

Compound that has a metal-carbon bond are called organometallic compounds. For example, alkyl magnesium halides (RMgX) are organometallic compounds because they have metal carbon bonds. Alkyl magnesium halides are also known as Grignard reagents. They are named after French Chemist Victor Grignard, who discovered them in 1900, and got Noble Prize in 1912. The Grignard reagents are used in the preparations of alkanes, alkenes, alcohols, aldehydes, ketones and carboxylic acids. Their general formula is RMgX. Where '*R*' is an alkyl or aryl group and '*X*' is chlorine, bromine or iodine.

17.2.1 Preparation of Grignard Reagents

Grignard reagents are prepared in the laboratory by the reaction of an alkyl or aryl halides with magnesium metal in the presence of pure diethyl ether in the absence of moisture, CO_2, or O_2.

$$R—X + Mg \xrightarrow{\text{Ether}} RMgX$$

$$CH_3—Cl + Mg \xrightarrow{\text{Ether}} CH_3—MgCl$$

17.2.2 Reactivity of Grignard Reagents

Grignard reagents are highly reactive compounds due to the presence of high polar carbon-magnesium bond. In alkyl magnesium halide, carbon is more electronegative than magnesium. Hence, carbon has partial negative charge and magnesium has partial positive charge.

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

The partial negative charge of carbon makes the alkyl group highly reactive towards electrophile and acts as a source of nucleophile.

The order of reactivity for various halides with same alkyl group to magnesium is as:

$RI > RBr > RCl$

Alkyl iodide is more reactive than alkyl bromide which in turn is more reactive than alkyl chloride.

The order of reactivity for the given halogen with various alkyl groups to magnesium is as:

$CH_3X > C_2H_5X > C_3H_7X$

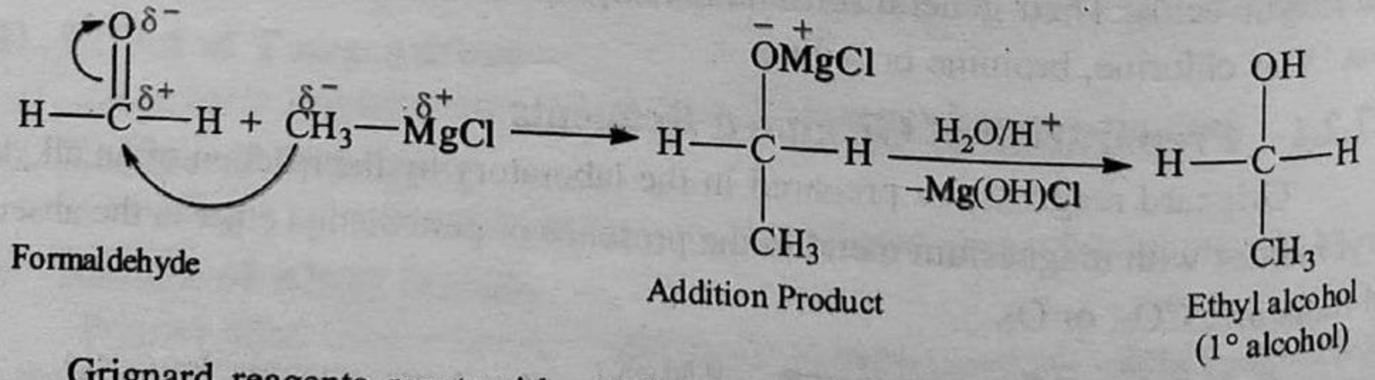
Methyl halide is more reactive than ethyl halide which in turn is more reactive than propyl halide.

17.2.3 Reactions of Grignard Reagents

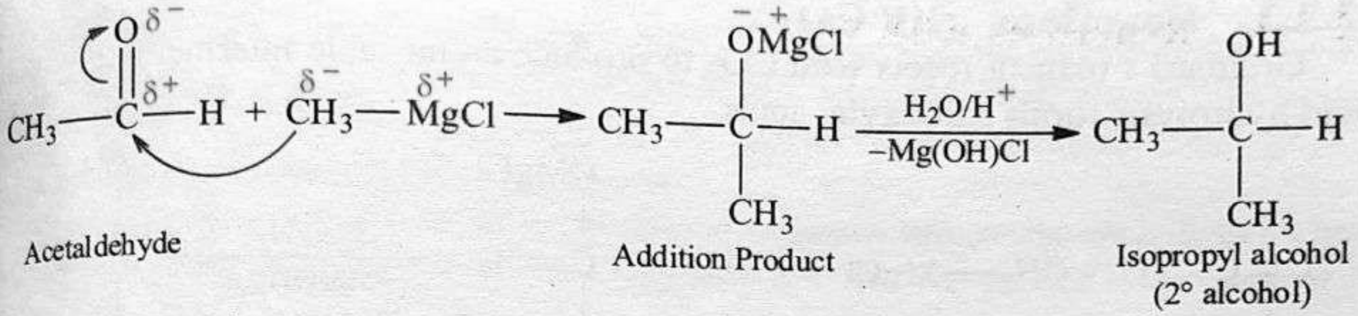
Grignard reagents react with organic and inorganic compounds to form a variety of valuable compounds.

17.2.3.1 Reactions with Aldehydes and Ketones

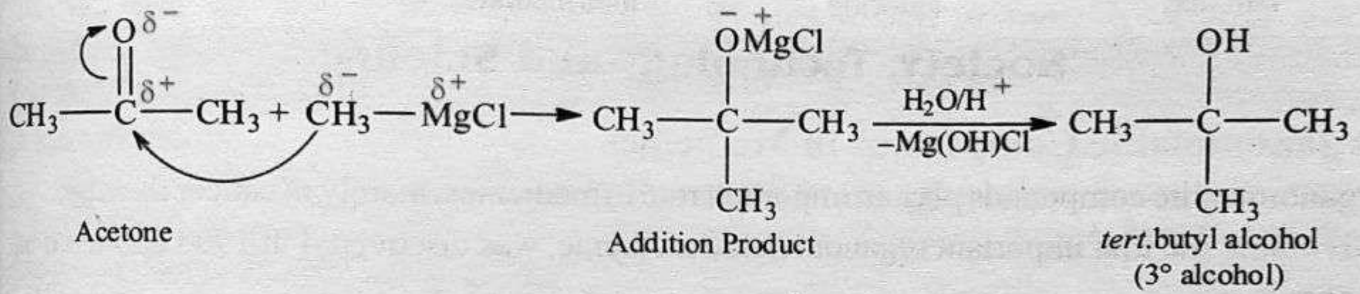
Grignard reagents react with formaldehyde to produce addition products which on acid hydrolysis form primary alcohols. This reaction can be used to increase the length of carbon chain.



Grignard reagents react with aldehydes other than formaldehyde to produce addition products which on acid hydrolysis form secondary alcohols.



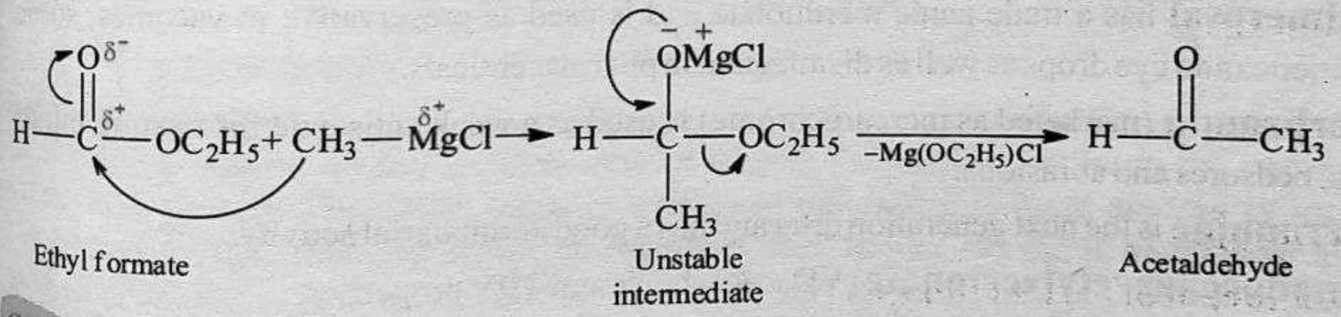
Grignard reagents react with ketones to produce addition products which on acid hydrolysis form tertiary alcohols.



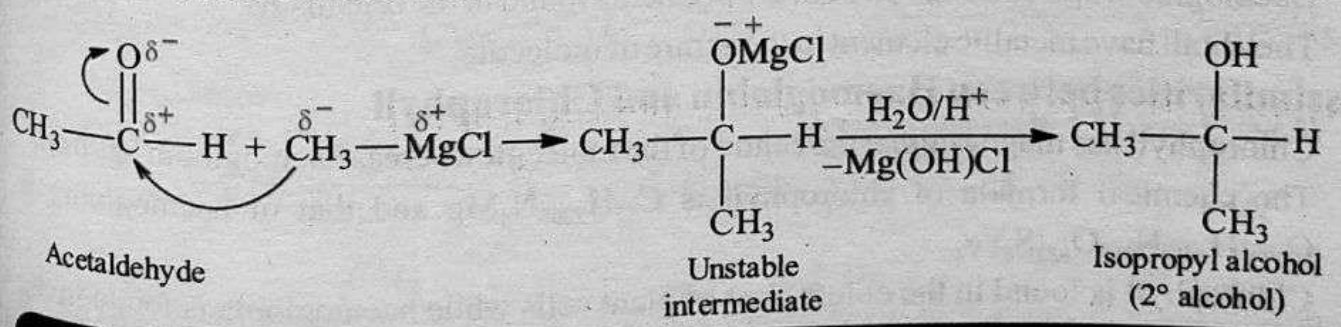
17.2.3.2 Reactions with Esters

It involves two steps:

Step 1: Ethyl formate reacts with Grignard's reagent to produce an unstable intermediate that expels an alkoxide ion in the ester to produce an aldehyde.



Step 2: The acetaldehyde reacts with a second molecule of the Grignard's reagent to produce an unstable intermediate which on acid hydrolysis forms secondary alcohol.

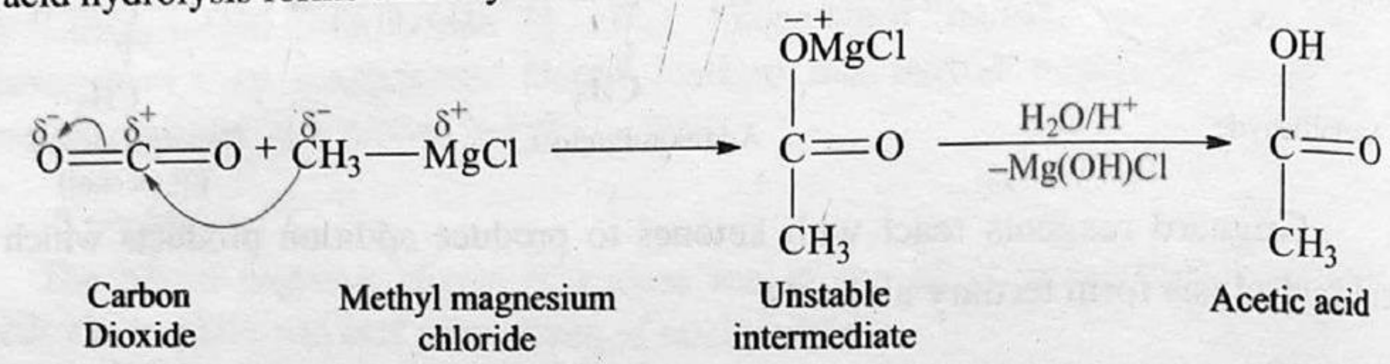


Keep in Mind

The esters, other than ethyl formate, reacts in the same way with an excess of Grignard's reagents to form tertiary alcohols.

17.2.3.3 Reactions with CO_2

Grignard's reagent reacts with CO_2 to produce an unstable intermediate which on acid hydrolysis forms carboxylic acids.



$$O=C=O + CH_3-MgCl \longrightarrow CH_3-C(=O)-\overset{-}{O}\overset{+}{Mg}Cl \xrightarrow[-Mg(OH)Cl]{H_2O/H^+} CH_3-C(=O)-OH$$

Society, Technology and Science

Organometallic Compounds in Medicines

Organometallic compounds play an important role in medicines, mainly in cancer therapy. Salvarsan, the first important organometallic medicine, was discovered in 1908 and used as an anti-syphilis.

Cisplatin is a chemotherapy drug and is highly effective in treating several cancers such as ovarian and testicular cancers.

Carboplatin is used to treat ovarian cancer.

Thimerosal has a trade name merthiolate and is used as preservative in vaccines, some cosmetics and eye drops as well as disinfectant in pharmaceuticals.

Merbromin (marketed as mercurochrome) is used as a weak antiseptic for treating minor cuts, bedsores and abrasions.

Ferroquine is the next generation drug and has a good antimalarial activity.

Vanadoceneacetylacetonate (VDacac) shows anti-HIV properties.

Comparison between Haemoglobin and Chlorophyll

- Haemoglobin and chlorophyll both are pigments found in the organisms.
- They both have metallic element in the centre of molecule.

Dissimilarities between Haemoglobin and Chlorophyll

- Chlorophyll has magnesiumat the centre of the moleculewhereas haemoglobin has iron.
- The chemical formula of chlorophyll is $C_{55}H_{7205}N_4Mg$ and that of haemoglobin is $C_{2952}H_{4664}N_{812}O_{832}S_8Fe_4$.
- Chlorophyll is found in the chloroplast of plant cells while haemoglobin is found in the blood of all vertebrates and some invertebrates.
- Chlorophyll gives green colour to the leaves, seaweed, algae and vegetables whereas haemoglobin gives red colour to the blood in the form of RBC.

- The main function for haemoglobin is to transport oxygen from the lungs to various parts of the body whereas the main function of chlorophyll is to absorb light energy from the sun and changes it into chemical energy by the process of photosynthesis. Chlorophyll is considered as the factory of oxygen on earth.

It is important to note that no life is possible on our planet without chlorophyll. Because of this chlorophyll is also known as the *blood of plants* just like haemoglobin is the blood of the body.

17.3 Amines

Amines are derivatives of ammonia in which one or more hydrogen atoms have been replaced by alkyl or aryl groups. Amines are classified as primary, secondary and tertiary, depending on the number of alkyl groups bonded to the nitrogen atom.

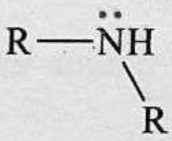
Primary amine has one alkyl group bonded to nitrogen atom. Secondary amine has two alkyl groups bonded to the nitrogen atom. Tertiary amine has three alkyl groups bonded to the nitrogen atom.

$\ddot{N}H_3$

Ammonia

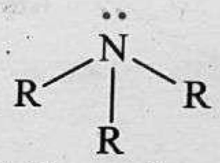
$R-\ddot{N}H_2$

Primary amine



$R-\ddot{N}H-R$

Secondary amine



Tertiary amine

17.3.1 Nomenclature

Common Names

Their common names are obtained by adding the suffix *amine* to the name of alkyl or aryl groups. The entire name is written as one word. If there are two or more alkyl or aryl groups, then the prefix di-, or tri- is used before the name of alkyl or aryl group. If there are two or more different alkyl or aryl groups, then the names of alkyl or aryl groups are arranged in alphabetical order. Examples are:

CH_3-NH_2

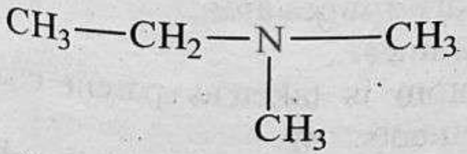
Methylamine

$CH_3-CH_2-NH_2$

Ethylamine

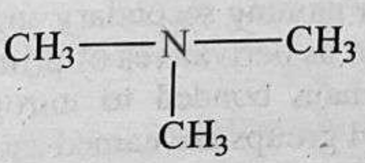
$CH_3-CH_2-NH-CH_3$

Ethylmethylamine



$CH_3-CH_2-N(CH_3)-CH_3$

Ethyldimethylamine



$CH_3-N(CH_3)-CH_3$

Trimethylamine

Keep in Mind

In common system, most of the primary amines are named as ***alkylamines***.

IUPAC Names

Amines are classified as primary, secondary or tertiary.

Primary Amines

The primary amines having more complex alkyl or aryl groups are generally named as ***alkanamines***. Main points for naming amines are:

i) Select the longest continuous chain of carbon atoms containing amino group and name it.

ii) Their names are obtained by replacing the ending –e of parent alkanes by adding the suffix *amine*.

iii) Number the parent chain from that end which is nearer to the functional group that is amino group.

iv) When another functional group is present in the compound, the amino group is generally listed as a substituent.

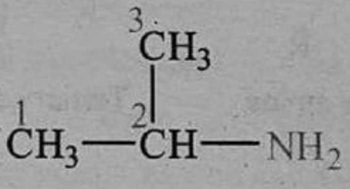
Examples are:

$CH_3—NH_2$

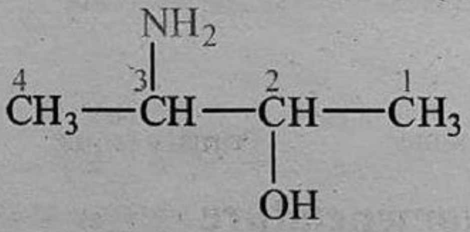
Methanamine

$CH_3—CH_2—NH_2$

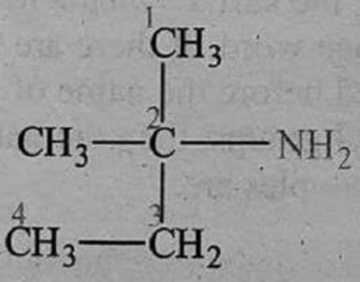
Ethanamine



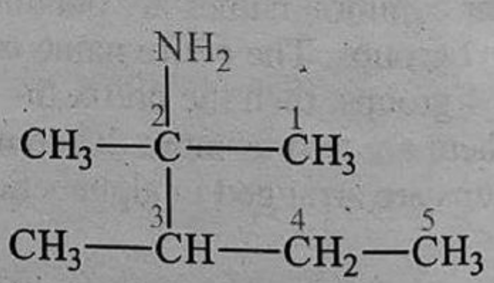
2-Propanamine



3-Amino-2-butanol



2-Methyl-2-butanamine



2,3-Dimethyl-2-pentanamine

Secondary and Tertiary Amines

Main points for naming secondary and tertiary amines are:

i) They are named as derivatives of primary amines.

ii) The longest chain bonded to nitrogen atom is taken as parent chain. The remaining alkyl groups are named as substituents.

iii) The locant *N* is used to designate the location of substituents bonded to a nitrogen atom of amino group.

iv) If the same alkyl groups appear more than once, then the prefix di or tri is used. If the amines have two or three different alkyl groups, then designate the groups individually in alphabetical order.

v) The secondary amines are generally named as ***N*-alkylalkanamines.**

vi) The tertiary amines are generally named as ***N,N*-dialkylalkanamines** (when both alkyl groups are the same) or as ***N*-alkyl-*N*-alkylalkanamines** (when both alkyl groups are different).

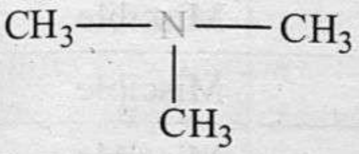
Examples are:

$CH_3-CH_2-NH-CH_3$

N-methylethanamine

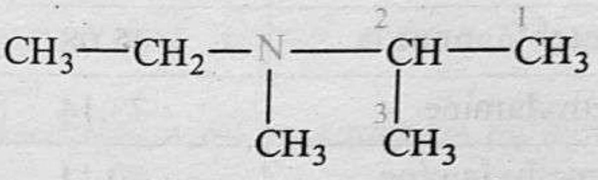
$CH_3-CH_2-NH-CH_2-CH_3$

N-ethylethanamine



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

N,N-dimethylmethanamine



$CH_3-CH_2-\underset{\underset{CH_3}{|}}{N}-\overset{2}{\underset{\underset{CH_3}{3|}}{CH}}-\overset{1}{CH_3}$

N-ethyl-N-methyl-2-propanamine

17.3.2 Physical Properties of Amines

Physical State

Lower amines are gases while higher amines with three or more carbon atoms are liquids and still higher ones are solids.

Odour

Methyl amine and ethyl amine have ammoniacal smell but higher amines have fishy smell.

Boiling Points

Amines are polar compounds. Polarity of amines is due to the presence of nitrogen atom. Both primary and secondary amines form intermolecular hydrogen bonds. The hydrogen bonds in alcohols are much stronger than amines as the oxygen of alcohols is more electronegative than the nitrogen of amines. Amines have higher boiling points than corresponding hydrocarbons and lower boiling points than those of corresponding alcohols or carboxylic acids. Tertiary amines do not form hydrogen bonds with each other, therefore their boiling points are similar to those of the corresponding alkanes.

Solubility

Lower amines are soluble in water due to formation of hydrogen bonds with water molecules. However, the solubility of amines decreases with increase in the size of alkyl group (hydrophobic part). Higher members of amines are predominantly insoluble in water. Amines are more soluble in water than corresponding alcohols and ethers. This may be due to the increased basicity of the amines.

Table 17.6: Physical Properties of Some Amines

Name	Molar Mass (g/mol)	Boiling Point (°C)	Solubility at 25°C in water
Methylamine	31.1	6	Miscible
Ethylamine	45.08	17	Miscible
Propylamine	59.11	48	Miscible
Butylamine	73.41	78	Miscible
Dimethylamine	45.08	7	Miscible
Diethylamine	73.14	56	Miscible
Trimethylamine	59.11	3	Miscible
Triethylamine	101.19	89	Slightly soluble

17.3.3 Structure of Amines

The nitrogen atom present in amines is sp^3 hybridized. The nitrogen atom has five electrons in the valence shell. It has three unpaired electrons and one lone pair of electrons. The three unpaired electrons form sigma bonds with hydrogen atoms or carbon atoms of alkyl groups. According to VSEPR theory, molecules having three bond pairs and one lone pair give trigonal pyramidal shapes. Hence, the structure of amines is trigonal pyramidal. The $C\widehat{N}C$ angle in amines is less than 109.5°. The angles in amines is approximately 108°.

17.3.4 Basicity of Amines

Amines are basic in nature due to the presence of lone pair of electrons on the nitrogen atom. Alkanamines are more basic than ammonia due to the presence of electron releasing alkyl groups. Alkyl groups concentrate the electron density of nitrogen and hence, make the lone pair of nitrogen more easily available for sharing with acids. Thus, the expected order of basicity of amines is: > 3° alkylamines > 2° alkylamines > 1° alkylamines.

The observed basicity of methylamine, dimethylamine and trimethylamine have been found to follow the expected order in gas phase. Conversely, they do not follow the expected trend of basicity order in aqueous solution and gets changed as:

$$(CH_3)_2NH\ (pK_b = 3.29) > CH_3NH_2\ (pK_b = 3.36) > (CH_3)_3N\ (pK_b = 4.28)$$

The larger the value of pK_b, the smaller is the tendency to accept a proton from water.

The basic strength of amines in aqueous solutions not only depends on electron releasing effect of alkyl groups but also depends on steric effect and hydration effect.

Due to high steric effect 3° alkylamine cannot donate electron to proton.

17.3.5 Preparation of Amines

Some of the methods for the preparation of amines are mentioned below:

17.3.5.1 Alkylation of Ammonia by Alkyl Halides

Alkyl halide reacts with aqueous or alcoholic solution of ammonia in a sealed tube on heating to produce primary, secondary and tertiary amines. This is a nucleophilic substitution reaction (S_N2 reaction).

The process of cleavage of the carbon-halogen bond by ammonia molecule is known as ***ammonolysis***.

$$NH_3 + CH_3I \longrightarrow CH_3NH_2 + HI$$

$$CH_3NH_2 + CH_3I \longrightarrow (CH_3)_2NH + HI$$

$$(CH_3)_2NH + CH_3I \longrightarrow (CH_3)_3N + HI$$

$$(CH_3)_3N + CH_3I \longrightarrow [(CH_3)_4\overset{+}{N}]\overset{-}{I}$$

Primary amine is the major product when ammonia is present in excess. Conversely, tertiary amine is the major product when alkyl halide is present in excess.

The resulting salt (methylammonium iodide) on treatment with a base regenerates amines.

$$[(CH_3)_4\overset{+}{N}]\overset{-}{I} + NaOH \longrightarrow (CH_3)_3N + NaI + CH_3OH$$

17.3.5.2 Reduction of Nitrogen containing Functional Groups

Amines are obtained by the reduction of nitrogen containing functional groups such as nitriles, nitro compounds and amides.

17.3.5.2.1 Reduction of Nitriles

Nitriles are reduced to primary amines by $LiAlH_4$ or catalytic hydrogenation.

$$\underset{\text{Methyl cyanide}}{CH_3CN} + 4[H] \xrightarrow{LiAlH_4} \underset{\text{Ethylamine}}{CH_3CH_2NH_2}$$

$$\underset{\text{Methyl cyanide}}{CH_3CN} + 2H_2 \xrightarrow{Ni} \underset{\text{Ethylamine}}{CH_3CH_2NH_2}$$

This method is used for increasing the length of carbon chain.

17.3.5.2.2 Reduction of Nitro Compounds

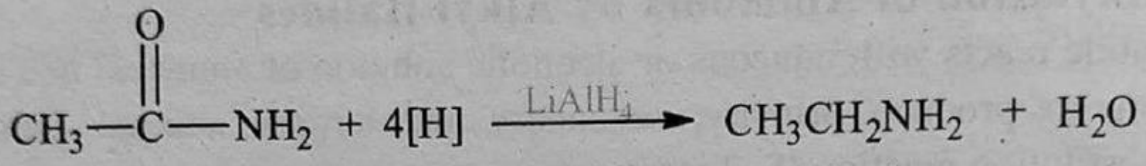
Nitro compounds are reduced to primary amines by $LiAlH_4$ or Zn/HCl or H_2/Ni or H_2/Pt.

$$\underset{\text{Nitromethane}}{CH_3NO_2} + 6[H] \xrightarrow{LiAlH_4} \underset{\text{Methylamine}}{CH_3NH_2} + 2H_2O$$

$$CH_3NO_2 + 3H_2 \xrightarrow{Pt} CH_3NH_2 + 2H_2O$$

17.3.5.2.3 Reduction of Amides

Amides are reduced to primary amines by $LiAlH_4$.



$$\underset{\text{Acetamide}}{CH_3-\overset{\overset{O}{\|}}{C}-NH_2} + 4[H] \xrightarrow{LiAlH_4} \underset{\text{Ethylamine}}{CH_3CH_2NH_2} + H_2O$$

17.3.6 Reactivity of Amines

Amines can act both as bases and nucleophiles. The main reactions of amines are due to the presence of a lone pair of electrons on nitrogen atom. These electrons attack the electron deficient centres (positive or slightly positive parts) of other molecules.

17.3.7 Reaction of Amines

17.3.7.1 Overview

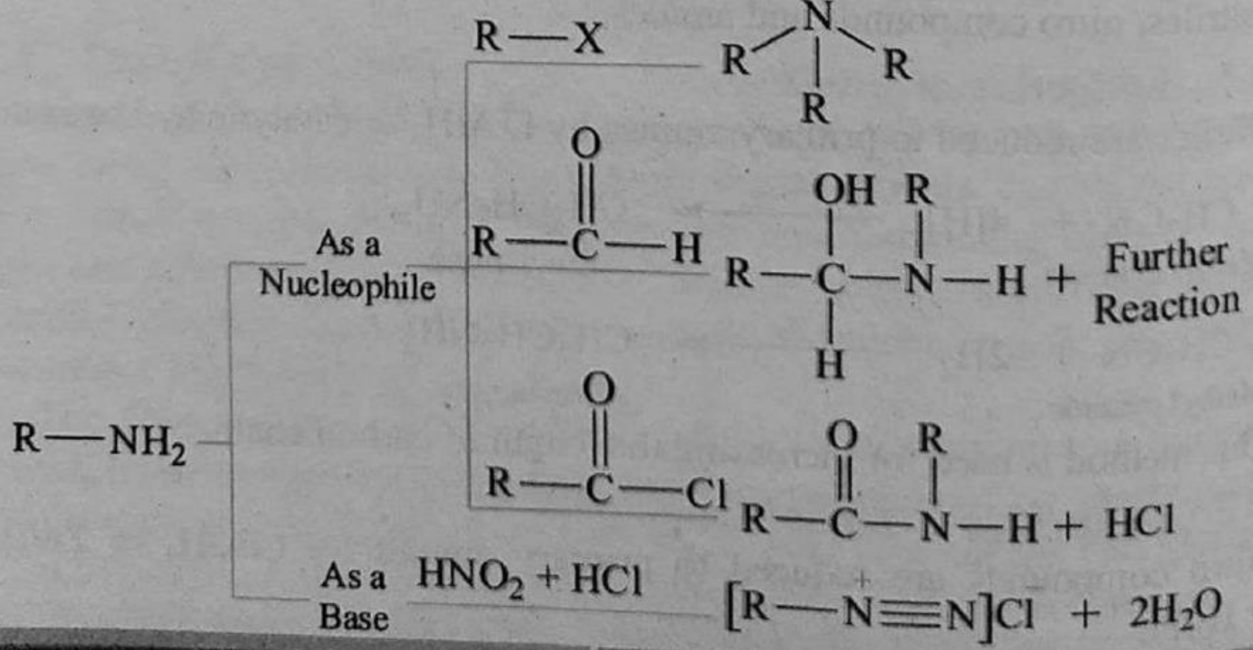
The important organic reactions of amines as nucleophiles are:

i) Amines are alkylated by alkyl halides through nucleophilic substitution.

ii) Amines reacts with alkyl halides through nucleophilic substitution to form a mixture of products.

iii) Amines reacts with acid halides (or acid anhydrides) through nucleophilic acyl substitution to form substituted amides.

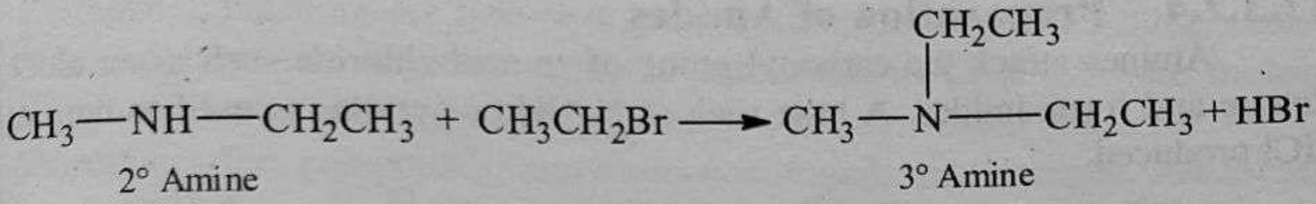
iv) Amines can also act as bases and react with nitrous acid to from diazonium salts.



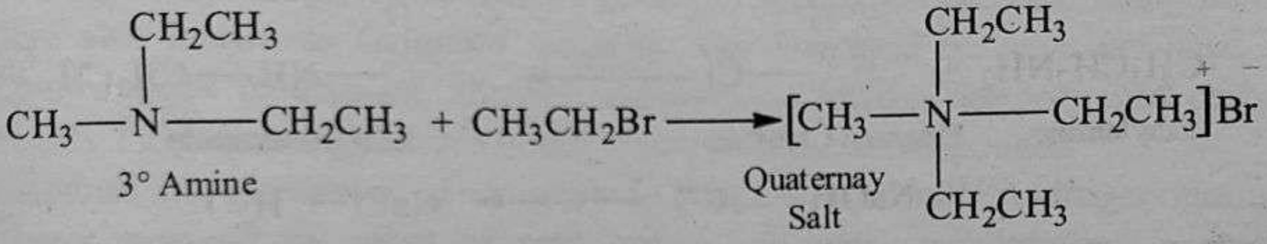
17.3.7.2 Alkylation of Amines by Alkyl Halides

Amines react with primary alkyl halides to form alkylated ammonium halides.

$$\underset{1^\circ\ \text{Amine}}{CH_3—NH_2} + CH_3CH_2Br \longrightarrow \underset{2^\circ\ \text{Amine}}{CH_3—NH—CH_2CH_3} + HBr$$



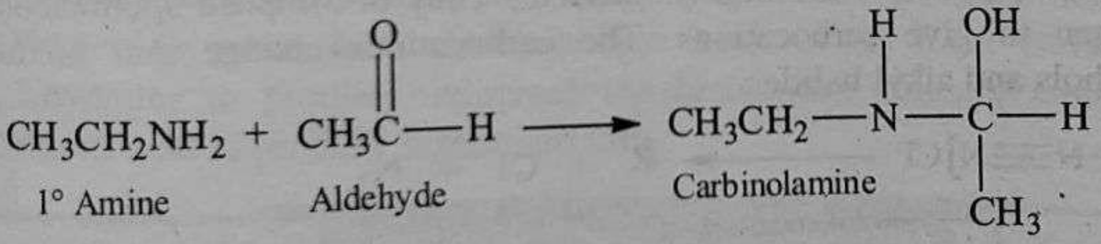
$$\underset{2^\circ\ \text{Amine}}{CH_3—NH—CH_2CH_3} + CH_3CH_2Br \longrightarrow \underset{3^\circ\ \text{Amine}}{CH_3—\overset{\overset{\displaystyle CH_2CH_3}{|}}{N}—CH_2CH_3} + HBr$$



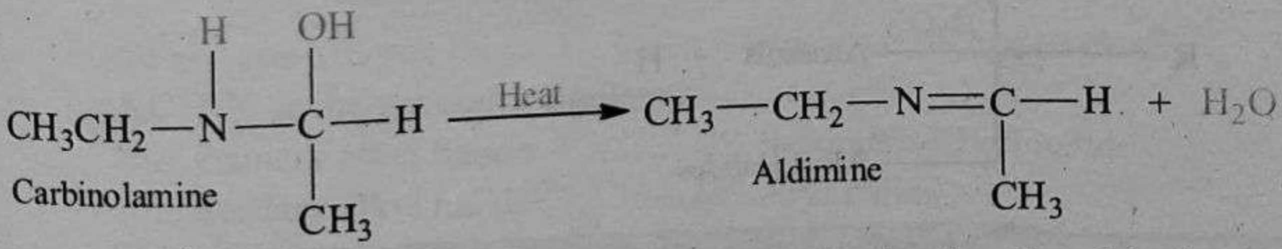
$$\underset{3^\circ\ \text{Amine}}{CH_3—\overset{\overset{\displaystyle CH_2CH_3}{|}}{N}—CH_2CH_3} + CH_3CH_2Br \longrightarrow \underset{\text{Quaternay Salt}}{\left[CH_3—\underset{\underset{\displaystyle CH_2CH_3}{|}}{\overset{\overset{\displaystyle CH_2CH_3}{|}}{N}}—CH_2CH_3\right]^{+}Br^{-}}$$

17.3.7.3 Reaction of Amines with Aldehydes and Ketones

Aldehydes react with primary amines to form carbinolamine that dehydrates to produce aldimines (Schiff's bases).

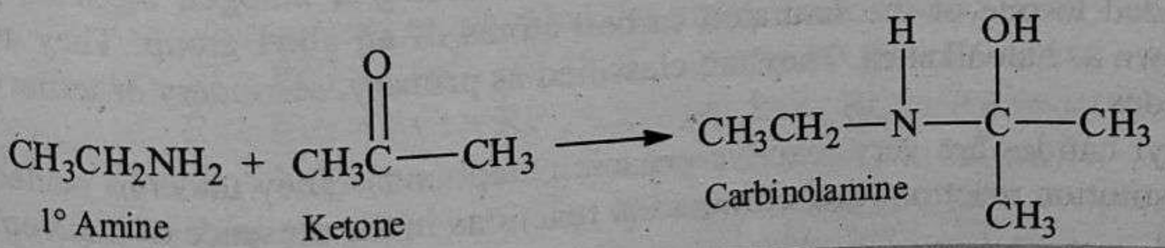


$$\underset{1^\circ\ \text{Amine}}{CH_3CH_2NH_2} + \underset{\text{Aldehyde}}{CH_3\overset{\overset{\displaystyle O}{\|}}{C}—H} \longrightarrow \underset{\text{Carbinolamine}}{CH_3CH_2—\overset{\overset{\displaystyle H}{|}}{N}—\underset{\underset{\displaystyle CH_3}{|}}{\overset{\overset{\displaystyle OH}{|}}{C}}—H}$$

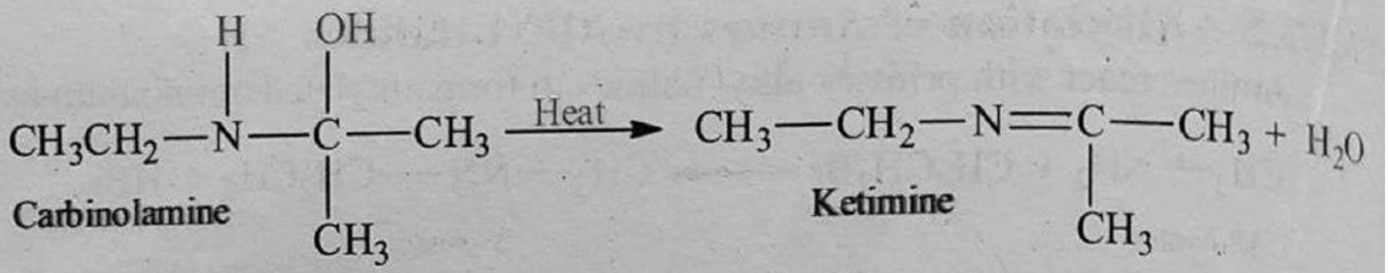


$$\underset{\text{Carbinolamine}}{CH_3CH_2—\overset{\overset{\displaystyle H}{|}}{N}—\underset{\underset{\displaystyle CH_3}{|}}{\overset{\overset{\displaystyle OH}{|}}{C}}—H} \xrightarrow{\text{Heat}} \underset{\text{Aldimine}}{CH_3—CH_2—N{=}\underset{\underset{\displaystyle CH_3}{|}}{C}—H} + H_2O$$

Ketones react with primary amines to form carbinolamine that dehydrates to produce ketimines (Schiff's bases).



$$\underset{1^\circ\ \text{Amine}}{CH_3CH_2NH_2} + \underset{\text{Ketone}}{CH_3\overset{\overset{\displaystyle O}{\|}}{C}—CH_3} \longrightarrow \underset{\text{Carbinolamine}}{CH_3CH_2—\overset{\overset{\displaystyle H}{|}}{N}—\underset{\underset{\displaystyle CH_3}{|}}{\overset{\overset{\displaystyle OH}{|}}{C}}—CH_3}$$

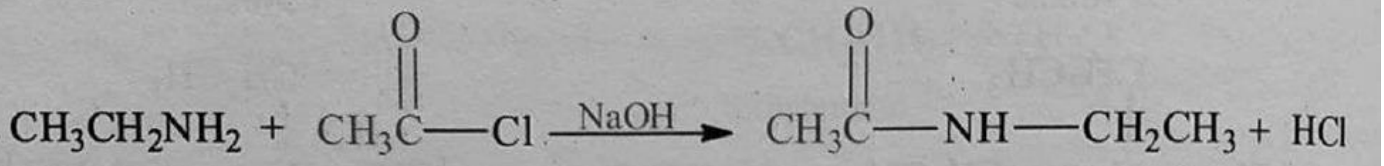


$$CH_3CH_2-\overset{H}{N}-\underset{CH_3}{\overset{OH}{C}}-CH_3 \xrightarrow{Heat} CH_3-CH_2-N=\underset{CH_3}{C}-CH_3 + H_2O$$

Carbinolamine Ketimine

17.3.7.4 Preparation of Amides

Amines attack the carbonyl group of an acid chloride such as an aldehyde or ketone and form amides. A base such as NaOH or pyridine is used to neutralize the HCl produced.



$$CH_3CH_2NH_2 + CH_3\overset{O}{\overset{\|}{C}}-Cl \xrightarrow{NaOH} CH_3\overset{O}{\overset{\|}{C}}-NH-CH_2CH_3 + HCl$$

Ethylamine **Ethanoyl Chloride** **Ethylethanamide**

$$NaOH + HCl \longrightarrow NaCl + H_2O$$

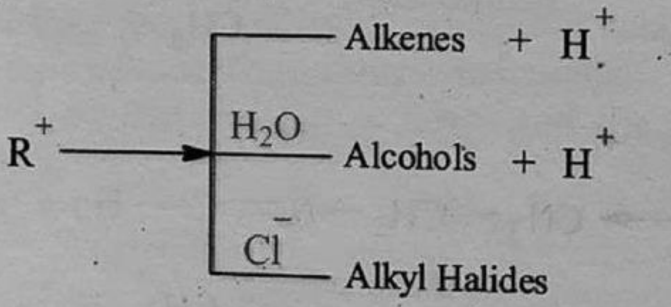
17.3.7.5 Preparation of Diazonium Salts

Amines react with nitrous acid to produce diazonium salts.

$$R-NH_2 + HNO_2 + HCl \longrightarrow [R-\overset{+}{N}\equiv N]\overset{-}{Cl} + 2H_2O$$

The diazonium salts are highly unstable. They decompose spontaneously by losing nitrogen to give carbocations. The carbocations change into mixtures of alkenes, alcohols and alkyl halides.

$$[R-\overset{+}{N}\equiv N]\overset{-}{Cl} \longrightarrow \overset{+}{R} + \overset{-}{Cl} + N_2$$



Summary of Facts and Concepts

- Alkyl halides are organic compounds containing a halogen atom covalently bonded to one of the saturated carbon atoms of an alkyl group. They are also known as haloalkanes. They are classified as primary, secondary or tertiary alkyl halides.
- Alkyl halides are very reactive organic compounds. They undergo nucleophilic substitution reactions and elimination reactions in the presence of nucleophile or base.

- Nucleophilic substitution reactions or S_N reactions are the reactions in which an electron rich nucleophile replaces another nucleophile to form a new molecule. In nucleophilic substitution reactions, the nucleophile is always Lewis base and it may be neutral or negatively charged. The substrate is frequently an alkyl halide and the leaving group is a halide ion.
- Elimination reactions are type of organic reactions in which two substituents are removed from two adjacent saturated carbon atoms of a substrate molecule. Elimination reactions occur simultaneously with substitution reactions.
- Organometallic compounds are those compounds that contain metal-carbon bonds. Alkyl magnesium halides (RMgX) are organometallic compounds and are also known as Grignard reagents. The Grignard reagents are used in the preparations of alkanes, alkenes, alcohols, aldehydes, ketones and carboxylic acids. Grignard reagents are highly reactive organic compounds.
- Amines are derivatives of ammonia in which one or more hydrogen atoms have been replaced by alkyl or aryl groups. Amines are classified as primary, secondary and tertiary. Amines can act both as bases and nucleophiles. The main reactions of amines are due to the presence of a lone pair of electrons on nitrogen atom.
- Amines react with primary alkyl halides to form alkylated ammonium halides. They also react with aldehydes (or ketones) to form carbinolamine that dehydrates to produce aldimines (or ketimines). Primary amines react with nitrous acid to produce diazonium salts.

Multiple Choice Questions

Select one answer from the given choices for each question:

i) RCH_2X is the general formula of:

(a) Primary alkyl halide (b) Secondary alkyl halide

(c) Tertiary alkyl halide (d) Aryl halide

ii) The formula of chloroform is:

(a) CCl_4 (b) $CHCl_3$

(c) CH_2Cl_2 (d) CH_3Cl

iii) The boiling point of alkyl halides are in the following order:

(a) RI > RCl > RBr > RF (b) RI > RBr > RF > RCl

(c) RI > RBr > RCl > RF (d) RF > RCl > RBr > RI

iv) The alkyl halide on which a nucleophile attacks is known as:

(a) Reagent (b) Substrate

(c) Electrophile (d) Both reagent and substrate

v) Alkyl halides are considered to be very reactive compounds because they have:
(a) an electrophilic carbon
(b) A nucleophilic carbon
(c) an electrophilic carbon and a good leaving group
(d) a nucleophilic carbon and a good leaving group

vi) Which statement is correct about carbocations?
(a) They are reactive species (b) They are stable species
(c) They are electron rich species (d) They have filled orbitals

vii) Which statement is true about bases?
(a) They are electron pair acceptor species.
(b) They can accept electrons from hydrogen
(c) Their strength is measured by rate constant
(d) Their strength is measured by base dissociation constant

viii) In S_N1 reactions, the rate of reaction depends upon the concentration of:
(a) One reactant molecule (b) Two reactant molecules
(c) Nucleophile (d) Both nucleophile and electrophile

ix) The S_N2 reactions can be best performed with:
(a) Primary alkyl halides (b) Secondary alkyl halides
(c) Tertiary alkyl halides (d) Aryl halide

x) Primary alcohol is obtained by the reaction of Grignard's reagent with:
(a) Aldehydes other than formaldehyde (b) Acetone
(c) Formaldehyde (d) Ethyl formate

Short Answer Questions

Q.1. What is the difference between a base and nucleophile?
Q.2. Can a good nucleophile be a strong base?
Q.3. Is iodine more nucleophilic than chlorine?
Q.4. What is a poor leaving group?
Q.5. The halogens are good leaving groups why?
Q.6 Why alkyl halides undergo nucleophilic substitution reaction?
Q.7. What is the carbocation intermediate?
Q.8 Do S_N2 reactions have carbocation intermediates?
Q.9. Why is a tertiary carbocation more stable than a secondary?
Q.10. Why are organometallic compounds important?
Q.11. What is the general formula of Grignard reagent? Give two examples of Grignard's reagents.

Q.12. Write the general equation for the preparation of Grignard reagents.

Q.13. What type of solvents can be used in Grignard reactions?

Q.14. Why is ether a good solvent for Grignard reactions?

Q.15. Why is a Grignard reagent so reactive?

Q.16. Is the carbon of Grignard's reagent electrophilic or nucleophilic?

Q.17. Define secondary amine and give two examples.

Q.18. Why do amines act as bases?

Q.19. Why aliphatic amines are more basic while aromatic amines are less basic than ammonia?

Long Answer Questions

Q.1. What are alkyl halides? Explain both the systems of nomenclature of alkyl halides.

Q.2. Draw structures for the following compounds.

i) Bromoethane
ii) Dichlorodibromomethane
iii) 2-bromo-3-chloropentane
iv) 1,1,2,2-tetrachloro-3,4-difluorohexane
v) 3-bromo-1-pentene

Q.3. Give common and IUPAC names to the following compounds:

i) CHI_3
ii) $CHCl_3$
iii) CH_3I
iv) $(CH_3)_2CHCl$
v) $(CH_3)_3CBr$

Q.4. Explain the structure and reactivity of alkyl halides.

Q.5. Write down three different methods for the preparation of alkyl halides. Which one is the best method for the preparation of alkyl halides?

Q.6. Write short note on the following:

i) Carbocations and their stability
ii) Nucleophile and base
iii) Substrate and leaving group

Q.7. What is the difference between S_N1 and S_N2 mechanisms?

Q.8. What are nucleophilic substitution reactions? Explain in detail the mechanism of nucleophilic substitution (S_N) reactions.

Q.9. What are β-elimination reactions? Explain the types and mechanism of elimination reactions.

Q.10. Discuss the factors that influence nucleophilic substitution and elimination reactions of alkyl halides.

Q.11. What are organometallic compounds? Discuss preparation and reactivity of Grignard's reagents.

Q.12. Explain important reactions of Grignard's reagent.

Q.13. What are amines? Explain nomenclature of amines.

Q.14. Draw structures for the following compounds.

i) 2-Methyl-2-propanamine
ii) 3-Methyl-2-hexanamine
iii) N-Methylethanamine
iv) N-Ethyl-3-hexanamine
v) N-Ethyl-N-methyl-2-butanamine

Q.15. Give common and IUPAC names to the following compounds:

i) CH_3NH_2
ii) $CH_3CH_2NH_2$
iii) $(CH_3)_2NH$
iv) $(CH_3)_3N$
v) $(CH_3)_2NCH_2CH_3$

Q.16. Discuss the structure, basicity and reactivity of amines.

Q.17. Write down methods for the preparation of amines.

Q.18. Describe physical and chemical properties of amines.