

Federal Board

Objective Chemistry

Part I & Part II

By

Same Authors

An Approach To Physics

(Subjective Book)

Part I & Part II

Conceptual Physics

(Objective)

Part I & Part II.

CHAPTER 17

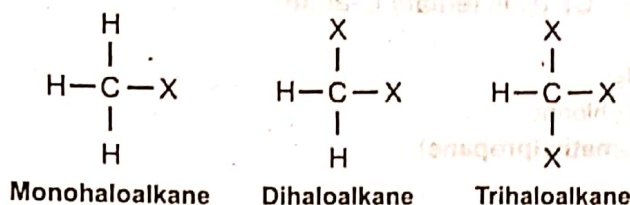
ALKYL HALIDES AND AMINES

Introduction

Haloalkanes

Halogen derivatives of alkanes are called haloalkanes.

They may be mono, di, tri or poly haloalkanes depending upon the number of halogen atoms present in the molecule.



Alkyl halides do not exist in nature. They are synthetic compounds and have oily nature.

Alkyl Halides

Monohaloalkanes are called alkyl halides or haloalkanes containing one halogen atom are called alkyl halides.

- Their general formula is $\text{C}_n\text{H}_{2n+1}\text{X}$.
- They are represented by $\text{R}-\text{X}$ where R may be methyl, ethyl, propyl, etc. and X represents halogen atom (F, Cl, Br or I).

Primary C-atom:

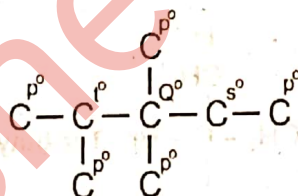
Carbon atom, directly attached to one or no carbon atom is called primary (p° or 1°) C-atom.

Secondary C-atom:

C-atom, directly attached to two C-atoms simultaneously is called secondary (s° or 2°) C-atom.

Tertiary C-atom:

C-atom, directly attached to three C-atoms simultaneously is called tertiary (t° or 3°) C-atom

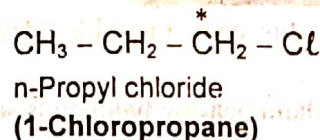
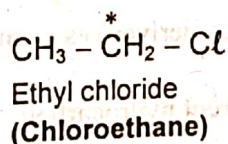
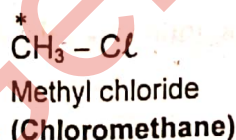


Classification of Alkyl Halides

Alkyl halides are classified into primary, secondary and tertiary alkyl halides.

(i) Primary Alkyl Halides:

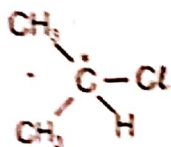
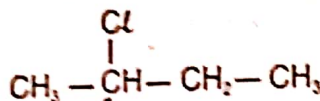
"Alkyl halides in which halogen atom is attached with primary carbon are called primary alkyl halide".



(* C is primary carbon atom)

(ii) Secondary Alkyl Halides:

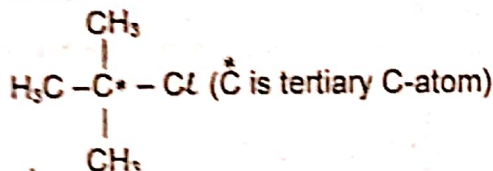
"Alkyl halides in which halogen atom is attached with a secondary carbon atom are called secondary alkyl halides."

Iso-Propyl chloride or
2-ChloropropaneSec-Butyl chloride or
2-Chlorobutane

(C is secondary carbon atom)

(iii) Tertiary Alkyl Halides:

"Alkyl halides in which halogen atom is attached to a tertiary carbon are called tertiary alkyl halide".



t-Butyl chloride

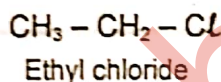
(2-Chloro-2-methylpropane)

Nomenclature

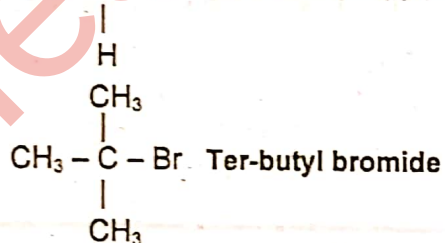
Alkyl halides are named according to the following systems:

(i) Common System of Naming

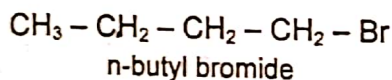
- The alkyl halides are named according to the nature of the alkyl group to which halogen atoms are attached.
e.g.



- For secondary alkyl halides, the prefix sec- and for tertiary alkyl halides, the prefix ter- or t- is added before the name of alkyl halides, e.g.

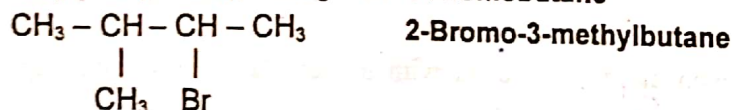
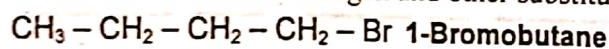


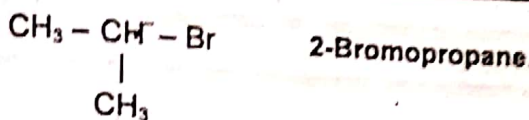
- When all the carbons of alkyl group of primary alkyl halides are in a straight chain, the prefix n- is used before the name which indicates 'normal'. e.g.

**(ii) IUPAC System of Naming**

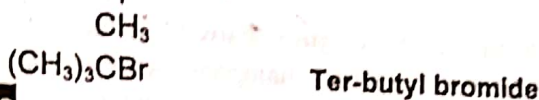
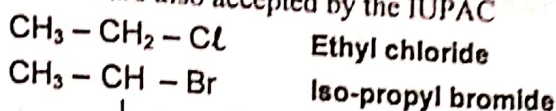
According to this system alkyl halides are named as derivatives of alkanes. The following rules are observed for this purpose:

- The longest chain bearing halogen is selected as parent hydrocarbon.
- Prefix 'halo' i.e., Chloro for Cl, Bromo for Br, etc, is used before the name of hydrocarbon.
- Positional numbers are used to indicate halogen and other substituent by the usual methods, e.g.,





The names given below are also accepted by the IUPAC

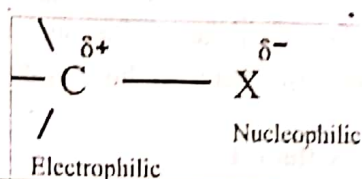


Physical Properties

The polar bond creates a molecular dipole that raises the melting points and boiling points compared to alkanes.

Structure

- The alkyl halide functional group consists of an sp^3 hybridized C atom bonded to a halogen, (X), via σ bond.
- The carbon halogen bonds are typically quite polar due to the high electronegativity and polarizability of the halogen.

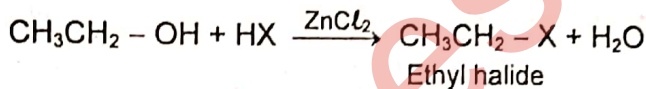


Exercise: Q.3 (ii) Give three methods for the preparation of alkyl halides.

Preparations of Alkyl Halides

(1) Reactions of Alcohols with Hydrogen Halides

Alcohols may be converted to the corresponding alkyl halides by the action of halogen acid in the presence of ZnCl_2 , which acts as a catalyst.

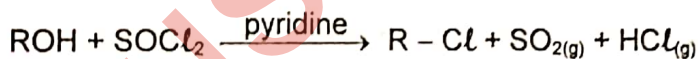


Lucas' reagent is a solution of zinc chloride in concentrated hydrochloric acid. This solution is used to distinguish alcohols.

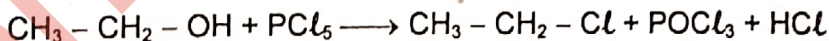
(2) Reaction of Alcohols with other Halogenating agents (SOCl_2 , PX_3 , PX_5)

- (a) Alcohols react with thionyl chloride (SOCl_2) in pyridine as a solvent to give alkyl chlorides.

This is the best method because HCl and SO_2 escape leaving behind the pure product.



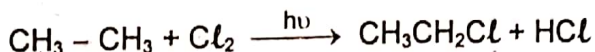
- (b) Phosphorous trihalides or phosphorous pentahalides react with alcohols to form alkyl halides.



Q. Which is the best method of preparing alkyl Halides?

(3) Halogenation of Alkanes

By the action of chlorine or bromine, alkanes are converted into alkyl halides. This reaction takes place in the presence of diffused sunlight or ultraviolet light.



Limitation:

This method does not give pure alkyl halides. Halogen derivatives containing two or more halogen atoms are also formed along with alkyl halides.

Exercise: Q.3(i) Discuss the reactivity of alkyl halides.

Reactivity of Alkyl halides

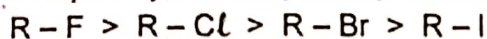
There are two main factors which control the reactivity of alkyl halides:

- (i) Bond polarity of C-X bond
- (ii) Bond energy of C-X bond

(i) Bond Polarity

The molecule of alkyl halide is polarized due to the greater electronegativity of halogens as compared to carbon. Hence carbon acquires partial positive whereas halogens acquires partial negative charge. Halogen becomes nucleophilic in character, which can be replaced by another nucleophile.

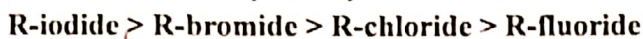
On the basis of bond polarity, reactivity of alkyl halides decreases in the following order:



(ii) Bond Energy

Experiments have shown that the bond energy of C-X bond is the main factor which decides the reactivity of alkyl halides, and not the polarity of the molecule.

A study of bond energies of C-X bond shows that C-F bond is the strongest. So the overall order of reactivity of alkyl halides is:



In fact the C-F bond is so strong that alkyl fluorides do not react under ordinary conditions.

Atom	E.N
F	4.0
Cl	3.0
Br	2.8
I	2.5
C	2.5
H	2.1

Bond	Bond Energy
C-F	467 kJ mol ⁻¹
C-Cl	346 kJ mol ⁻¹
C-Br	290 kJ mol ⁻¹
C-I	228 kJ mol ⁻¹
C-H	413 kJ mol ⁻¹

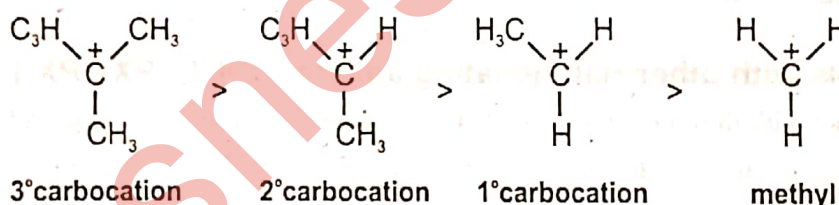
Important Concepts

Carbocations and their Stability

Organic species in which carbon bears +ive charge is called carbocation.

Stability:

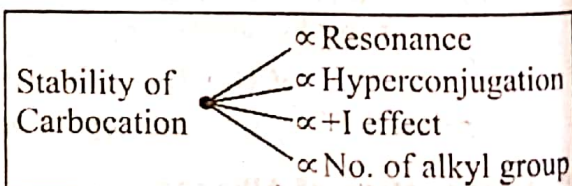
The general stability order of simple alkyl carbocations is: (most stable) 3° > 2° > 1° > methyl (least stable)



This is because alkyl groups are weakly electron donating due to hyperconjugation and inductive effects. Resonance effects can further stabilize carbocations when present.

Reactions involving carbocations:

1. Substitutions via the S_N1
2. Eliminations via the E1
3. Additions to alkenes and alkynes
4. Electrophilic substitution of aromatic compounds.



Nucleophiles and Bases

- It is species rich in electron.
- It has an unshared pair of electrons available for bonding.
- In most cases it is basic (acts as base).
- It may be negatively charged or neutral.

Examples of Nucleophiles:

HO^-	Hydroxide ion	Cl^-	Chloride ion
$\text{C}_2\text{H}_5\text{O}^-$	Ethoxide ion	Br^-	Bromide ion
HS^-	Hydrogen sulphide ion	NH_3	Ammonia
SCN^-	Thiocyanate ion	CN^-	Cyanide ion
$\text{H}_2\ddot{\text{O}}$	Water	I^-	Iodide ion
NH_2^-	Amino group		

Electrophile

- It is a species which attracts electrons (electron loving).
- In most cases, it is acidic in character.
- The carbon atom of an alkyl group attached with the halogen atom and bearing a partial positive charge is called an electrophile or electrophilic center.
- An electrophile may be neutral or positively charged.

Examples: AlCl_3 , BF_3 , Cl^+ , Br^+ , NO_2^+ , SO_3 , R^+ etc.

Substrate and Leaving Group

Substrate Molecule:

The alkyl halide molecule on which a nucleophile attacks is called a substrate molecule.

Leaving Group (LG):

- Leaving group is also a nucleophile.
- It departs with an unshared pair of electrons.
- The incoming nucleophile must be stronger than the departing one.

Examples:

Good Leaving Groups	Poor Leaving Groups	Good Leaving Group & Good nucleophile
Cl^- , Br^- , I^- , HSO_4^-	OH^- , OR^- , NH_2^-	I^- (Iodide ion)

Nucleophile	Electrophile
<ul style="list-style-type: none"> • Negatively charged ions (anions) are nucleophiles. e.g. Cl^-, H^-, Br^-, SO_4^{2-} etc • Neutral molecules in which central atom have lone pairs of electrons. e.g. PCl_3, PH_3, SO_2, NH_3, $\text{H}_2\ddot{\text{O}}$ etc. • Lewis bases are usually nucleophiles. • The molecules which contain pi electrons in their structures act as nucleophiles. e.g. ethene, benzene etc. 	<ul style="list-style-type: none"> • Positively charged ions (cations) are electrophiles. e.g. H^+, Cl^+, Br^+ • Neutral molecules in which central atom is electron deficient. e.g. BH_3, BF_3, BeCl_2, AlCl_3, ZnCl_2, FeCl_3 etc. • Lewis acids are usually electrophiles. • Neutral molecules in which central atom contains partial positive charge act as electrophiles. e.g. PCl_5, SO_3, CO_2 etc.

Iodide ion is a good nucleophile because of high polarizability and a good leaving group because of low bond energy.

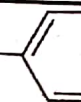
NUCLEOPHILIC SUBSTITUTION REACTIONS OF ALKYL HALIDES

- Alkyl chlorides, bromides and iodides are good substrates for nucleophilic substitution reactions.
- A variety of nucleophiles can be used to generate a range of new functional groups.

Nucleophilic Substitution Reactions

The following diagram reflects some of the more important reactions you may encounter.

Q. What does the term "nucleophilic substitution" imply?

Excellent	CH_3 -  - SO_3^- , NH_3
Very Good	I^- , H_2O
Good	Br^-
Fair	Cl^-
Poor	F^-
Very Poor	HO^- , NH_2^- , RO^-

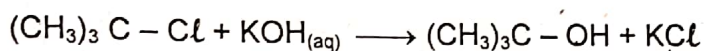
But water itself, is a good leaving group, since it is the conjugate base of H_3O^+ .

Exercise: Q.3(iii) Explain in detail $\text{S}_{\text{N}}1$ and $\text{S}_{\text{N}}2$ reactions with mechanism.

$\text{S}_{\text{N}}1$ MECHANISM

"The nucleophilic substitution reaction mechanism in which breaking of C-X bond and the formation of C-Nu bond occur one after the other in two different steps is called $\text{S}_{\text{N}}1$ reaction."

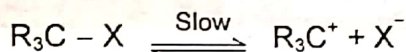
Example:



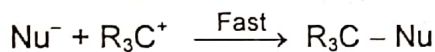
IUPAC designation = $\text{D}_{\text{N}} + \text{A}_{\text{N}}$
 D_{N} = Departure of nucleophile
 A_{N} = Addition of nucleophile

Explanation:

- (i) The substrate $\text{R}_3\text{C} - \text{X}$ first ionizes reversibly into R_3C^+ and X^- ions. This slow step is rate determining step.



- (ii) Then the carbocation combines with the attacking nucleophile to form product.

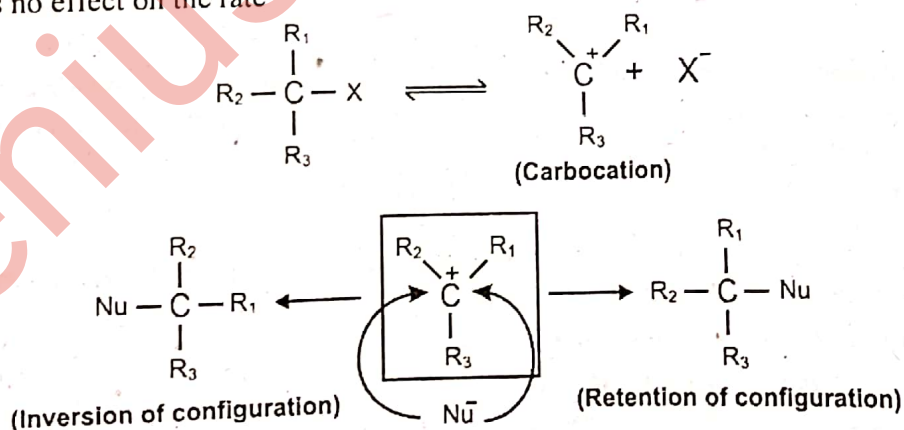


Mechanism:

Since only one molecule is undergoing a change in covalency in rate determining step, this two steps nucleophilic substitution reaction is unimolecular and is called $\text{S}_{\text{N}}1$ reaction. The brief mechanistic picture of $\text{S}_{\text{N}}1$ reaction base upon the following evidences:

(i) Kinetic evidence:

The rate of an $\text{S}_{\text{N}}1$ reaction depends upon the concentration of alkyl halide only. The change in concentration of attacking nucleophile has no effect on the rate



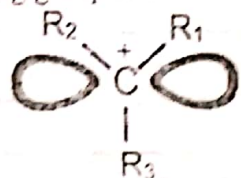
$$\text{Rate} = k[\text{R}_3\text{C} - \text{X}]$$

It is because the nucleophile combines with the carbocation in the second step. For the same reason, the rate of an $\text{S}_{\text{N}}1$ reaction does not depend on the nature of attacking nucleophile.

(ii) Stereo chemical evidence:

Experiments have shown that S_N1 reaction occurs with partial racemization. The extent of partial racemization depends upon several factors including stability of carbocation.

The carbon atom of carbocation is sp^2 hybridized and carries one empty p-orbital. The nucleophile can attack itself to the p-orbital either on the right or on the left side of carbon with equal ease. The expected product is a racemic mixture. However, the partial racemization suggests a different way of attachment, e.g., in case of unstable carbocation, the attack of nucleophile is greater from the side opposite to that of leaving group. Thus the side of carbon atom to which the leaving group is attached is somewhat shielded from the attack of nucleophile. The attack of nucleophile occurs more often on the side opposite to the side to which leaving group is attached, leading to partial inversion of configuration.

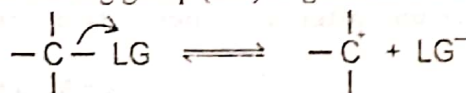


(Planer Carbocation)

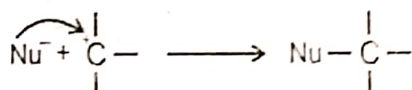
Therefore, the product has some optical activity.

(iii) Steps involved in S_N1 Reaction

Step 1: Slow loss of the leaving group (LG) to generate a carbocation intermediate.



Step 2: Rapid attack of a nucleophile on the electrophilic carbocation to form a new σ bond.

 **S_N2 MECHANISM**

"The nucleophilic substitution reaction mechanism in which breaking of C - X bond and the formation of C - Nu bond occur simultaneously in one step is called S_N2 reaction."

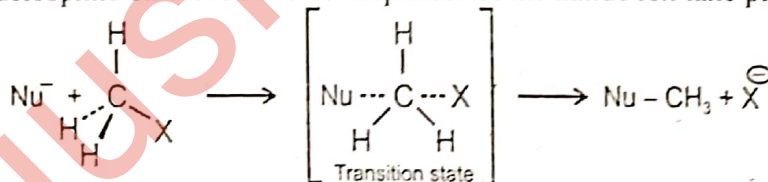
Example:



IUPAC designation = D_NA_N
Concerted reaction

Mechanism:

The attack of nucleophile on carbon and the departure of the halide ion take place simultaneously in single step.



- This is rate-determining step because the bond breaking and bond making processes occur simultaneously.
- Since two molecules are undergoing change in covalency in rate determining step, it is a bimolecular nucleophilic substitution reaction which is taking place in one step.

This mechanistic picture is based upon the following evidences.

(i) Kinetic evidence:

The rate of an S_N2 reaction depends upon the concentration of nucleophile as well as the concentration of alkyl halide. The rate expression for the reaction can be written as:



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

Where k = specific rate constant.

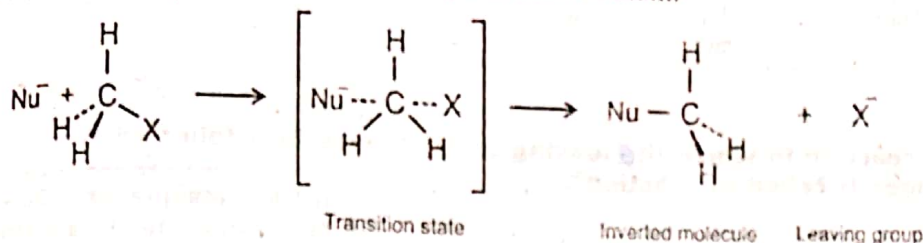
This means that the rate of reaction will be double if the concentration of any of the two is double.



The rate of reaction increases when concentration of either HO^- or CH_3-Br is increased.

(ii) Stereo chemical evidence:

A bimolecular nucleophilic substitution always occurs with inversion of configuration. The carbon atom in transition state is sp^2 -hybridized and is planar. The attacking nucleophile and the leaving groups are present in the transition state on opposite sides of electrophilic carbon atom.



Attacking nucleophile and LG must be antiperiplanar in transition state

Q. Which kind of S_N reactions are carried out by secondary alkyl halides?

Comparison of S_N1 and S_N2 Mechanism

S_N1	S_N2
• It is a two steps mechanism.	• It is a single (concerted) step mechanism.
• First step is slow one and second is fast.	• It has only one step and that is slow.
• It is a unimolecular reaction.	• It is a bimolecular reaction.
• It is favoured in polar solvents.	• It is favoured in non-polar solvents.
• Mostly tertiary alkyl halides give this reaction.	• Mostly primary alkyl halides give this reaction.
• 50 % inversion and 50% retention of configuration takes place.	• 100% inversion of configuration takes place.
• Rate = $k[R_3C - X]$	• Rate = $k[Nu][R - X]$

Exercise: Q.3(iv) What are β -elimination reactions? Explain them with detail.

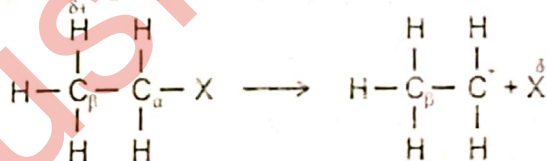
ELIMINATION REACTIONS**Elimination Reaction:**

"The chemical reaction in which two groups are eliminated from two adjacent atoms is called elimination reaction."

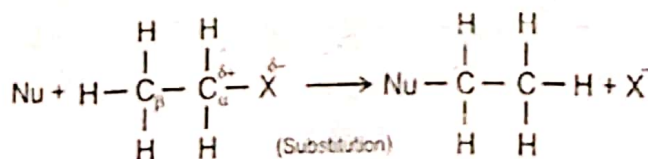
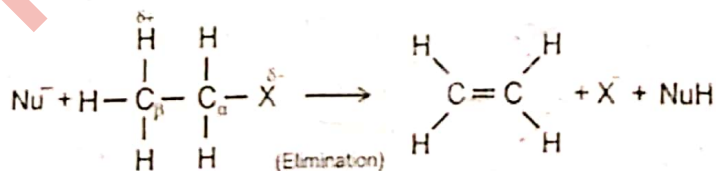
Since β -hydrogen is necessary for eliminations, it is also called β -elimination.

Explanation:

β -hydrogen atom in alkyl halides is slightly acidic due to electron withdrawing effect of halogen.

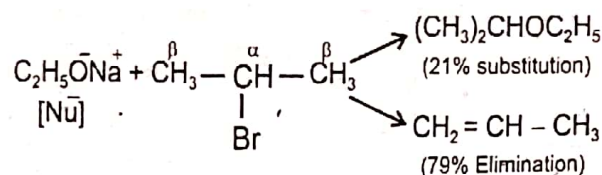


The attacking nucleophile can either attack α -carbon to give substitution product or β -hydrogen to give elimination reaction.



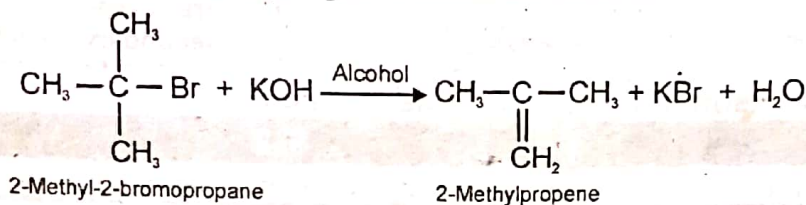
Note: • Strong bases such as OH^- , OR^- , NH_2^- cause elimination in preferences to substitution.

- Highly polarizable nucleophile and weak bases such as I^- , RS^- etc. give substitution reactions.



E1 Reaction

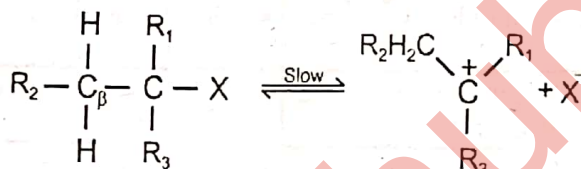
"Two steps elimination reaction in which the leaving group leaves first followed by the removal of hydrogen is called E1 reaction".



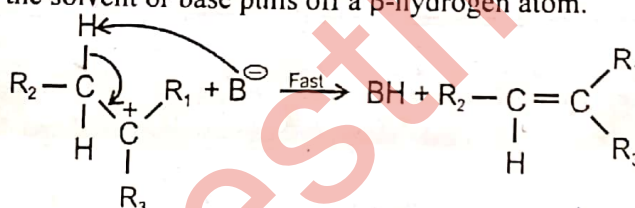
IUPAC designation = $D_N + D_H$
 D_N = Departure of nucleophile
 D_H = Departure of H-atom

Explanation:

- (i) The substrate undergoes slow ionization in the first step to form carbocation. This step is reversible and rate determining.



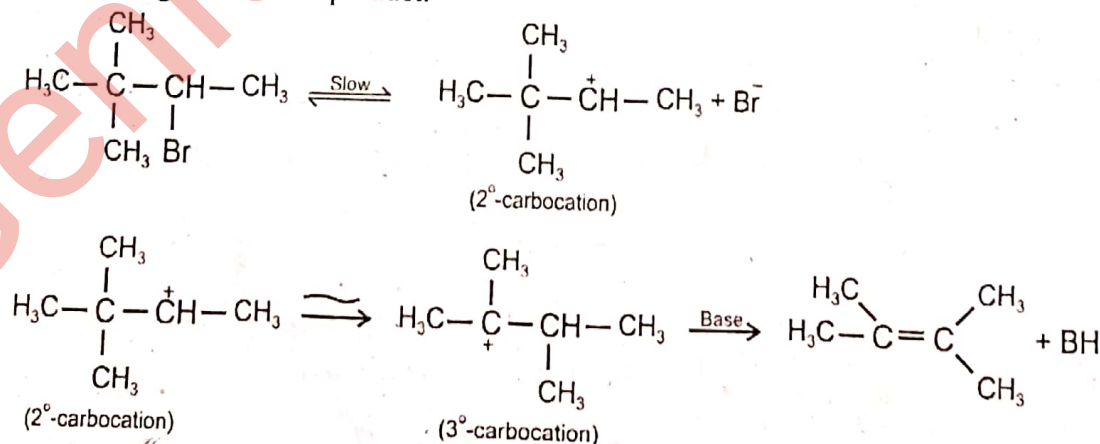
- (ii) In the second step the solvent or base pulls off a β -hydrogen atom.



- (iii) Since only one molecule is undergoing a change in the rate determining step, i.e., first step, this is a unimolecular elimination reaction.
- (iv) The E1-mechanism has been supported by the study of the reaction. It follows first order kinetics, in which rate of reaction depends only on the concentration of substrate.

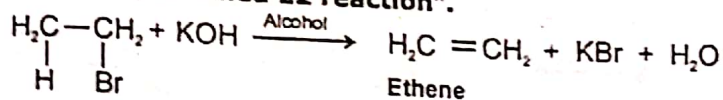
$$\text{Rate} = k[R_3C - X]$$

- (v) The presence of carbocation as an intermediate has been indicated by the presence of more than one kind of elimination products. A relatively less stable carbocation rearranges to give more stable carbonium before giving elimination product.



E2 Reaction

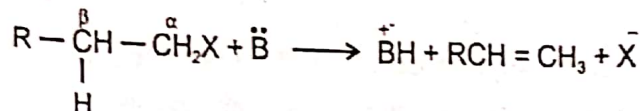
"One step elimination reaction in which both the atoms or groups leave simultaneously is called E2 reaction".



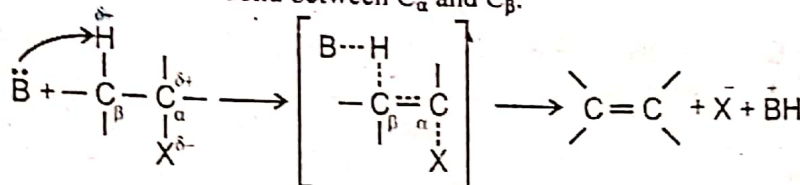
IUPAC designation = $\text{D}_\text{N}\text{D}_\text{H}$
 D_N = Departure of nucleophile
 D_H = Departure of H-atom

Explanation:

(i) Consider the reaction,



(ii) The attacking base removes a proton (H^+) from the β -carbon and the loss of halide ion simultaneously with the formation of double bond between C_α and C_β .



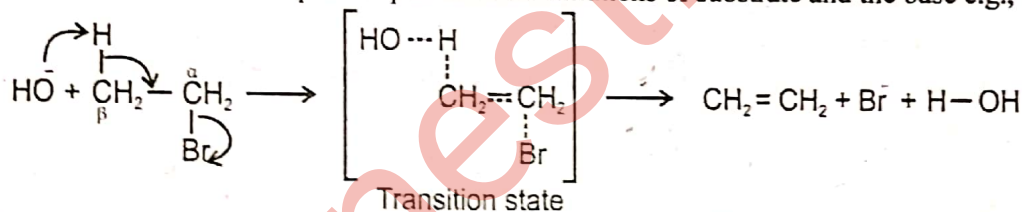
This is rate determining step because bond breaking and bond making processes are taking place simultaneously.

(iii) Since two molecules undergo a change in transition state, it is a bimolecular one step elimination reaction. Thus E2 is a one step process in which both the substrate and the base participate.

(iv) The observed rate law for E2-reaction is

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

(v) The rate of E2-reaction depends upon the concentrations of substrate and the base e.g., for the reaction.



(vi) The rate of reaction follows second order kinetics.

$$\text{Rate} = k[\text{CH}_3\text{CH}_2\text{Br}][\text{OH}^-]$$

Q. Differentiate between nucleophilicity and basicity.

Substitution versus Elimination Reactions

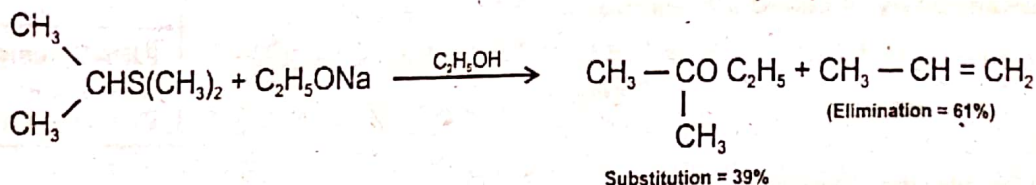
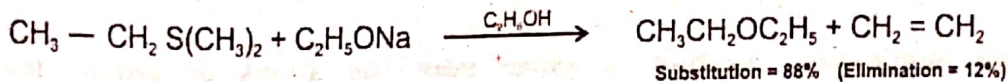
Though substitution and elimination reaction lead to different products, there is always a competition between them because of close resemblance in their mechanism. Since substitution is energetically more favorable, it is the dominant reaction in the substitution-elimination reaction.

- Elimination occurs only in the presence of β -Hydrogen where substitution reactions do not require this condition to be satisfied.

The following factors help to compare these two path ways:

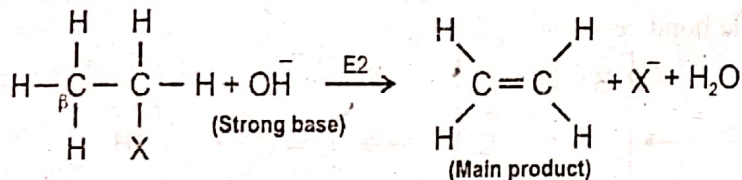
(i) Structure of Substrate:

Crowding within the substrate favors elimination over substitution because the approach of the nucleophile to α -carbon is difficult for substitution. Similarly the elimination is favorable because the removal of β -H atom by base from tertiary planar carbocation is easy, e.g.,

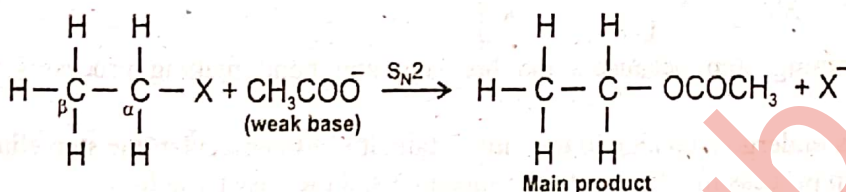


(ii) Nature of base:

When the electron pair donor is a strong base, e.g., OH^- , OR^- , NH_2^- etc, the dominant reaction is E_2 , while $\text{S}_{\text{N}}2$ reaction is a side reaction. However, when the nucleophile is a weak base like X^- , RS^- , etc the main reaction will be $\text{S}_{\text{N}}2$ while E_2 will be minor side reaction.

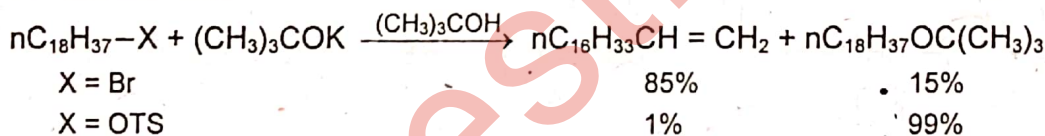


Strong base favours E_2 while strong nucleophile favours $\text{S}_{\text{N}}2$



(iii) The Nature of leaving group:

The role of leaving groups in elimination reactions is similar to that in substitution reactions. In unimolecular reactions ($\text{S}_{\text{N}}1$ and E_1), it does not affect the mechanism because both the elimination and substitution products are decided with carbocation. However, in the bimolecular reactions ($\text{S}_{\text{N}}2$ and E_2) the nature of product greatly depends upon the nature of leaving group. e.g.,



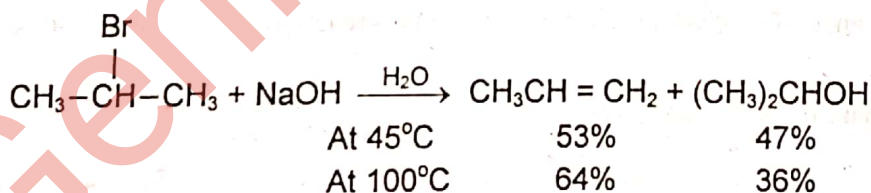
(iv) Nature of solvent

Elimination is favored more than substitution by decreasing the solvent polarity. Thus, alcoholic KOH promotes elimination while more polar aqueous KOH is used for substitution. E_1 and $\text{S}_{\text{N}}1$ are favored by polar solvents. In non-polar solvents, the reaction will follow E_2 -mechanism.

(v) Effect of Temperature

An increase in temperature will favor elimination more than substitution, because substitution reaction involves less reorganization of bonds as compared to eliminations. e.g.

Bimolecular Reaction:



Q. What is the effect of solvent nature on unimolecular and bimolecular S_{N} or E reactions?



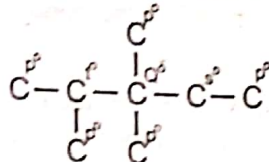
1. What are monohaloalkanes?

Ans. The haloalkanes containing one halogen atom are called monohaloalkanes or alkyl halides. Their general formula is $\text{C}_n\text{H}_{2n+1}\text{X}$.

Examples: $\text{CH}_3 - \text{CH}_2 - \text{Cl}$ $\text{CH}_3 - \text{CH}_2 - \text{CH}_2 - \text{Cl}$
 Chloroethane 1-Chloropropane

2. What are primary, secondary and tertiary carbon atoms?

Ans. Primary C-atom: Carbon atom directly attached to one or no carbon atom is called primary (p° or 1°) C-atom.
 Secondary C-atom: C-atom, directly attached to two C-atoms simultaneously is called secondary (s° or 2°) C-atom.
 Tertiary C-atom: C-atom, directly attached to three C-atoms simultaneously is called tertiary (t° or 3°) C-atom



Carbonium ion is not a suitable term. It should be carbocation.

3. What is carbonium ion?

Ans. An organic ion in which carbon bears positive charge is called carbonium ion or carbocation. e.g. R_3C^+ , R_2HC^+ , H_3C^+ etc.

- In carbocation, C is sp^2 hybridized
- It has planer structure.
- Order of stability of carbocation is $\text{R}_3\text{C}^+ > \text{R}_2\text{CH}^+ > \text{R}-\text{CH}_2^+ > \text{CH}_3^+$

4. What is leaving group?

Ans. Leaving group (LG) is also a nucleophile. It is called leaving group because it departs with an unshared pair of electrons.



5. What is sp^3 hybridization?

Ans. In sp^3 hybridization, one s and three p atomic orbitals (slightly differ in energy) intermix to form four equivalent orbitals called sp^3 hybrid atomic orbitals. e.g. in methane (CH_4), carbon is sp^3 hybridized.

6. Define bond polarity.

Ans. When two atoms are covalently bonded, the more electronegative atom draws the shared pair of electrons towards itself, thus causing bond polarity. The higher the polarity, the higher would be the reactivity of the molecule.

7. Define bond energy.

Ans. "The average amount of energy required to break all bonds of a particular type in one mole of the substance is called the bond energy."

When a bond is formed between two atoms, energy is released. The same amount of energy is absorbed when the bond is broken to form neutral atoms. It is determined experimentally, by measuring the heat involved in a chemical reaction. It is also called bond enthalpy, as it is a measure of enthalpy change at 298K.

8. What is nucleophilic reagent?

Ans. Nucleophilic Reagent:

- Negatively charged ions (anions) are nucleophiles. e.g. H^- , Cl^- , Br^- , SO_4^{2-} etc.
- Neutral molecules in which central atom have lone pairs of electrons.
e.g. PCl_3 , PH_3 , SO_2 , NH_3 , H_2O etc.
- Lewis bases are usually nucleophiles.
- The molecules which contain pi electrons in their structures act as nucleophiles. e.g. ethene, benzene etc.

9. What is electrophilic reagent?

Ans. Electrophilic Reagent:

- Positively charged ions (cations) are electrophiles. e.g. H^+ , Cl^+ , Br^+ etc.

- Neutral molecules in which central atom is electron deficient. e.g. BH_3 , BF_3 , BeCl_2 , AlCl_3 , ZnCl_2 , FeCl_3 etc.
- Lewis acids are usually electrophiles.
- Neutral molecules in which central atom contain partial positive charge act as electrophiles. e.g. SO_3 , PCl_5 , CO_2 etc.

10. Define Inductive effect.

Ans. An inductive effect is an electronic effect due to the polarization of σ bonds within a molecule or ion. This is typically due to an electronegativity difference between the atoms at either end of the bond.

11. Define resonating effect.

Ans. The electron displacement through covalent bonds determines the polarity of the molecule which in turn affect the physical properties of the molecule. The displacement of electrons at any number of p atomic orbitals is called resonating effect.

12. What is racemization?

Ans. Racemization is the conversion of an optically active substance into an optically inactive mixture of equal amounts of the dextrorotatory and levorotatory forms. Conversion of an optically active substance to a raceme.

13. Define transition state.

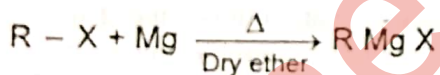
Ans. The highest energy structure along the reaction coordinate between reactants and products for every step of a reaction mechanism is called transition state. The species at this state is called activated complex.

ORGANOMETALLIC COMPOUNDS (GRIGNARD'S REAGENTS)

Exercise: Q.3(vi) Discuss the preparation and reactivity of Grignard's reagent.

Preparation of Grignard's Reagents

Magnesium metal (cut into small pieces) is added to a solution of an alkyl halide or aryl halide in only dry ether. The reaction mixture is heated with electric heater in a round bottom flask fitted with condenser and other arrangement to avoid the contact of moisture or oxygen.



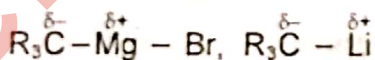
Alkyl bromides are generally used in the preparation of Grignard's reagent because of its intermediate reactivity. When alkyl halides are used, the solvent is either the high boiling solvent such as tetrahydrofuran is employed when less reactive aryl halides are used. Alkyl magnesium halides are not isolated but are used as ethereal layers.

Reactivity

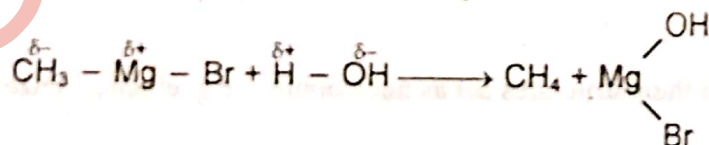
- Organo metallic compounds are nucleophile because of partial negative charge on the carbon of alkyl group. e.g.



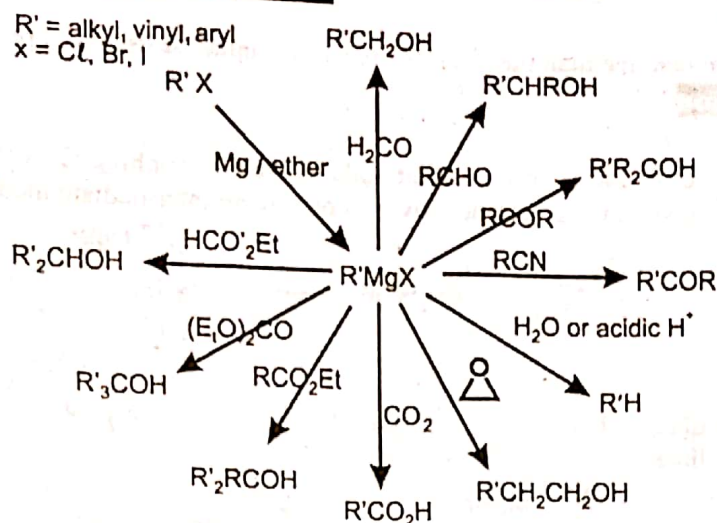
- Carbon atom being more electronegative than metals such as Mg, Li etc. The alkyl group as a whole bears partial negative charge and organo metallic compounds act as source of nucleophile, e.g.



- The following reaction supports the electrophilic character of organo metallic compounds.



Reactions of Grignard's Reagents



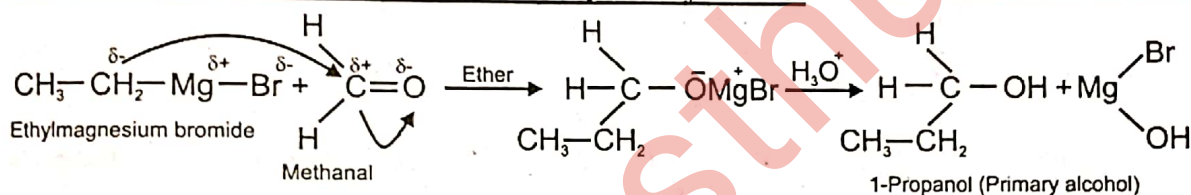
(1) With Aldehydes and Ketones

This is done in following three steps to produce primary, secondary and tertiary alcohols. These reactions are carried in the presence of ether followed by H_3O^+ . First two reactions are with aldehydes while third belongs to ketones.

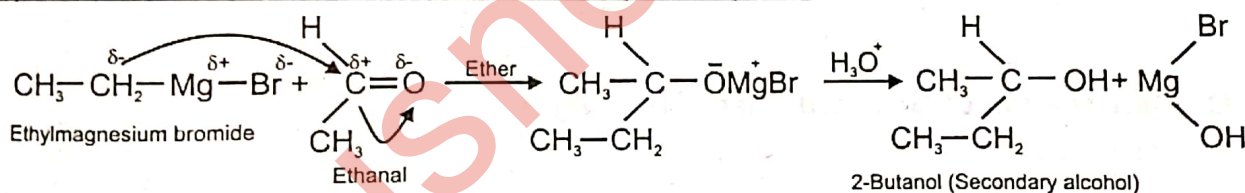
Alcohols having one - OH group are called monohydric alcohols. These are classified as:

- (i) Primary alcohols
- (ii) Secondary alcohols
- (iii) Tertiary alcohols

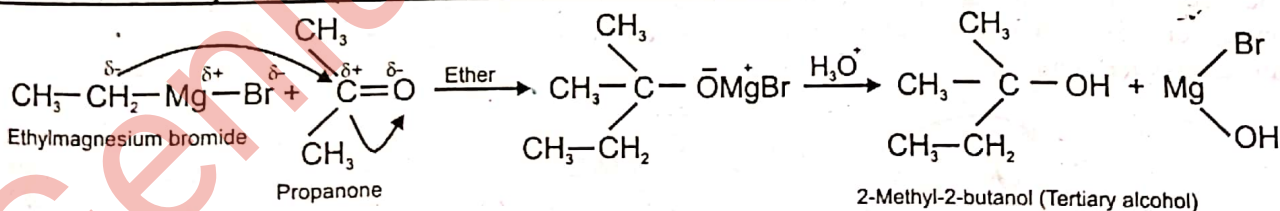
(i) Reaction with Methanal (Aldehyde) to form primary alcohol



(ii) Reaction with Ethanal (Aldehyde) to form secondary alcohol



(iii) Reaction with Propanone (Ketone) to form tertiary alcohol



Reaction type: Nucleophilic acyl substitution then nucleophilic addition

(2) Reactions of RLi or RMgX with an ester

- (i) Carboxylic esters, (RCO_2R) react with 2 equivalents of organolithium or Grignard reagents to give tertiary alcohols.
- (ii) The tertiary alcohol contains 2 identical alkyl groups.

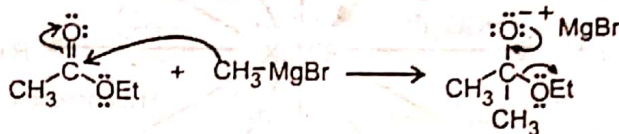
(iii) The reaction proceeds via a ketone intermediate which then reacts with the second equivalent of the organometallic reagent.

(iv) Since the ketone is more reactive than the ester, the reaction cannot be used as a preparation of ketones.

Steps involve during reaction

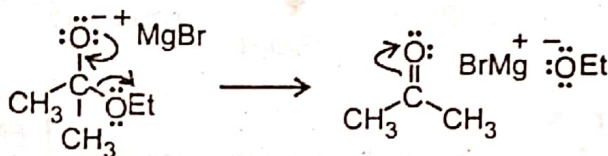
Step 1:

The nucleophilic C in the organometallic reagent adds to the electrophilic C in the polar carbonyl group of the ester. Electrons from the C = O move to the electronegative O creating an intermediate metal alkoxide complex.



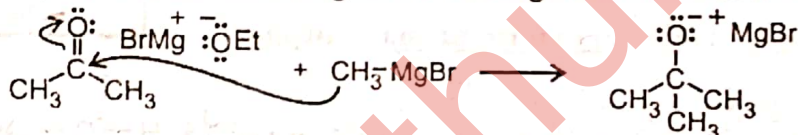
Step 2:

The tetrahedral intermediate collapses and displaces the alcohol portion of the ester as a leaving group, this produces a ketone as an intermediate.



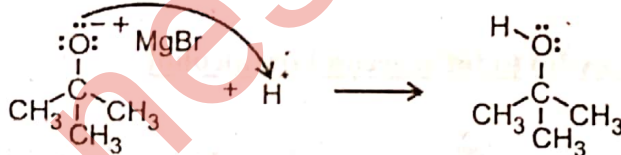
Step 3:

The nucleophilic C in the organometallic reagent adds to the electrophilic C in the polar carbonyl group of the ketone. Electrons from the C = O move to the electronegative O creating an intermediate metal alkoxide complex.



Step 4:

This is the work-up step, a simple acid / base reaction. Protonation of the alkoxide oxygen creates the alcohol product from the intermediate complex.

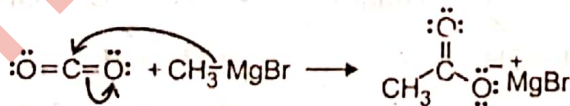


(3) With CO₂ (Carbonylation of Grignard Reagents, RMgX)

Nucleophilic addition of RMgX to CO₂

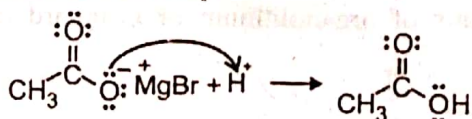
Step 1:


The nucleophilic C in the Grignard reagent adds to the electrophilic C in the polar carbonyl group, electrons from the C = O move to the electronegative O creating an intermediate magnesium carboxylate complex.



Step 2:

This is the work-up step, a simple acid/base reaction. Protonation of the carboxylate oxygen creates the carboxylic acid product from the intermediate complex.


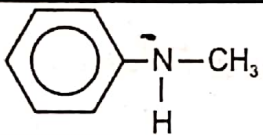
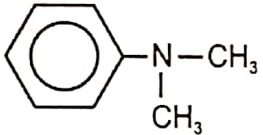
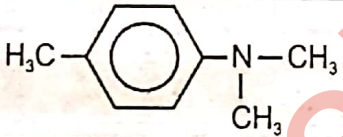


$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3 - \text{N} - \text{CH}_3 \end{array}$	Trimethyl amine (a ter-amine)
	Pyridine (a ter-amine)

(2) IUPAC System of Naming

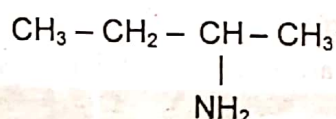
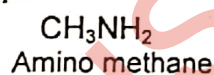
Aromatic compounds:

- Aniline, $\text{C}_6\text{H}_5\text{NH}_2$ containing methyl group on the ring is called Toluidine.
- If there is some alkyl group substituted in $-\text{NH}_2$ its name is represented by writing N-(alkyl group). It indicates that alkyl group is located on N-atom and not on the ring.
- If there are two substituents on N, it is repeated twice.

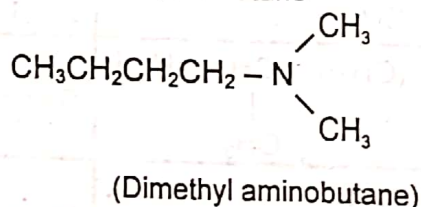
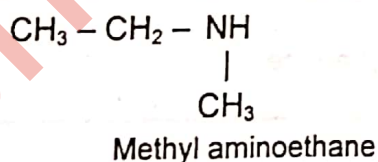
Structure	IUPAC Name
	p-Toluidine
	N-methyl aniline
	N,N-dimethyl aniline
	N,N-dimethyl p-toluidine

Aliphatic compounds:

- In this system amino group is indicated by a prefix-amino followed by name of hydrocarbons.
- The position of amino group is indicated by a number obtained by numbering the chain of hydrocarbon.
- Secondary and tertiary amines are named by using a compound prefix that includes the names of all but the largest alkyl group.

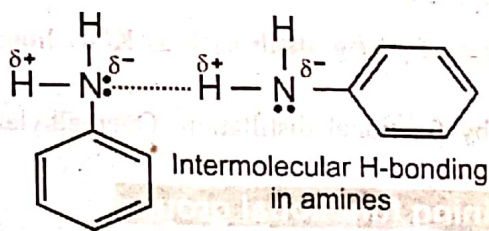


2-Aminobutane



Physical Properties

- The polar nature of the N - H bond (due to the electronegativity difference of the two atoms) results in the formation of hydrogen bonds with other amine molecules, or other H-bonding systems like water.

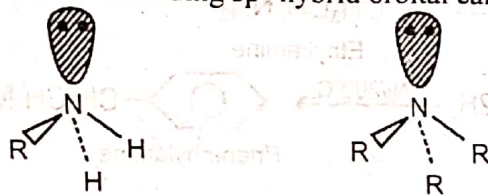


The applications of this are:

- They have high melting and boiling points compared to analogous alkanes.
- They have high solubility in aqueous media.

Structure

In amines, nitrogen atom is sp^3 -hybridized and has nearly tetrahedral structure. It forms three sigma bonds with its three sp^3 -hybrid orbitals while the fourth non-bonding sp^3 -hybrid orbital carries a lone pair of electrons.

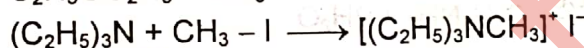
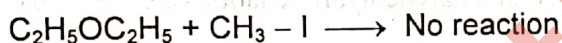


(Optically active tertiary amines)

The non-bonding electron pair (lone pair) is extremely important in explaining the chemical behavior of amines because it is responsible for the basic and nucleophilic properties of these compounds. An amine with three different groups is optically active.

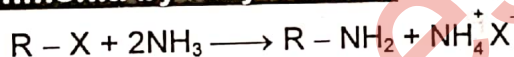
Basicity

Amines may act as bases towards acids and as nucleophiles towards electrophiles. They are more basic than alcohols and ethers and they are also more nucleophilic, e.g., ether does not react where as at the same temperature amines gives addition product with $CH_3 - I$,

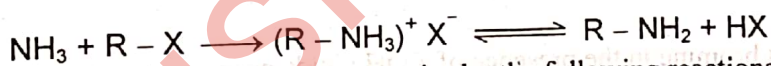


Preparation of Amines

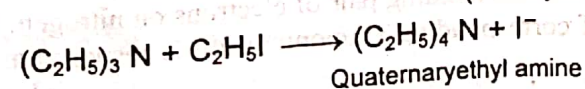
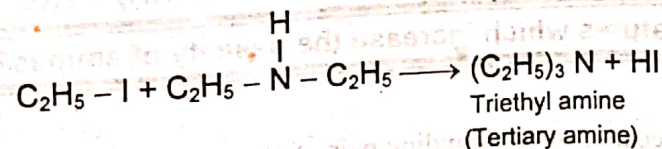
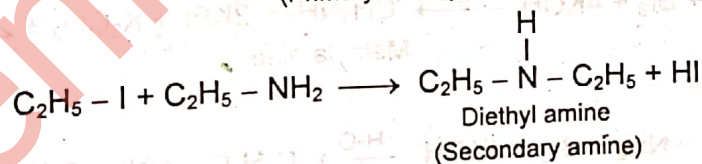
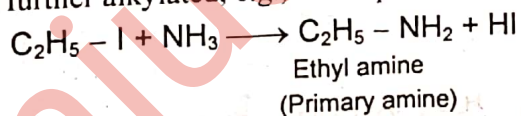
(1) Alkylation of Ammonia by Alkyl Halides



When an alcoholic or aqueous solution of ammonia is heated with an alkyl halide, a mixture of prim-, sec-, ter- amines and a quaternary ammonium salt is obtained. The reaction occurs with nucleophilic displacement of halide by ammonia of amines.



This reaction is further alkylated, e.g., accompanies by the following reactions.



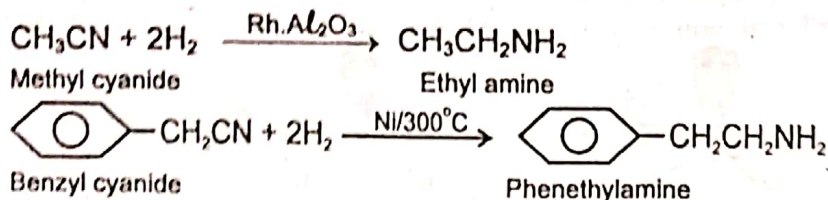
At the end of the reaction, addition of strong alkali such as KOH liberates free amines from their salts but the quaternary salt is unaffected.

- The three amines are separated by fractional distillation. Over alkylation can be avoided by using excess of ammonia but the yield is low.

Reductions of nitrogen containing functional groups

(i) Reduction of Nitriles

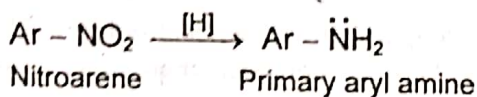
Reduction of alkyl or aryl nitriles gives primary amines. The reduction may be brought about by LiAlH_4 or sodium in ethanol. Catalytic hydrogen with $\text{Rh} - \text{Al}_2\text{O}_3$, Pt or Raney nickel may also be employed to get primary amines.



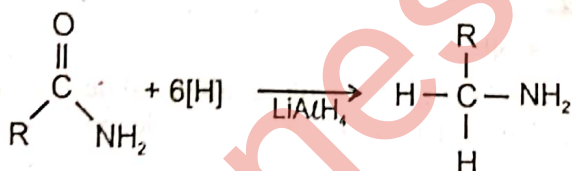
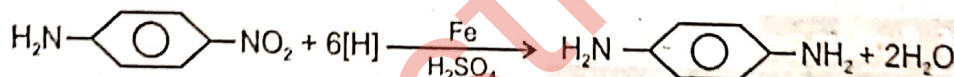
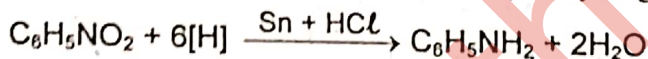
(ii) Reduction of Nitro Compounds

Nitro compounds on catalytic or chemical reduction produce primary amines.

- Nitroarenes can be reduced to primary aryl amines.



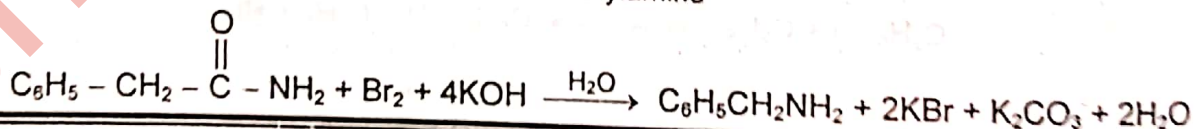
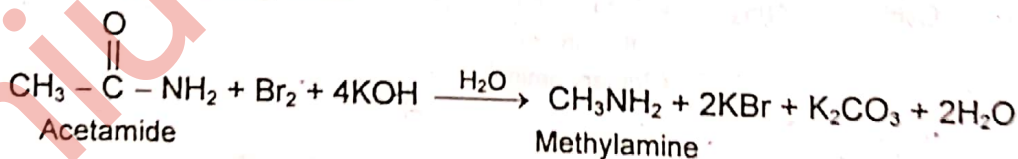
Typical reducing agents include Fe / H^+ , Sn / H^+ or catalytic hydrogenation (e.g. H_2 / Pd).



(iii) Reduction of Amides

An amide on treatment with bromine in the presence of KOH yields primary amines.

The reaction occurs through rearrangement.



MCCQ

Which amine is formed by the reduction of alkyl nitriles?

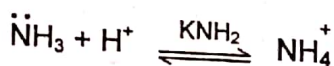
- (a) Primary amines (b) Secondary amines
(c) Tertiary amines (d) Quaternary ammonium salt

Exercise: Q.3(viii) What are the main features which increase the basicity of amines?

Basicity of Amines

Amines are bases and nucleophiles because of non-bonding pair of electrons on nitrogen. The relative availability of this pair of electron and the relative stability of corresponding ammonium ion is responsible of basicity of different amines.

Consider the following reactions:



- The strength of a base is expressed in terms of pK_b , i.e., $\text{pK}_b = -\log K_b$
- For ammonia and methyl amine, the pK_b values are:

$$\text{pK}_{b\text{NH}_3} = 4.76; \text{pK}_{b\text{CH}_3\text{NH}_2} = 3.38$$

Since $\text{pK}_{b\text{NH}_3} > \text{pK}_{b\text{CH}_3\text{NH}_2}$, methyl amine is a stronger base than ammonia.

Q. Why $\text{CH}_3 - \text{NH}_2$ is a stronger base than NH_3 ?

Ans. (i) Availability of electron pair

In ammonia, the pair of electrons attracted by s-orbitals of hydrogen atoms where as in $\text{CH}_3\text{-NH}_2$, sp^3 -orbital of carbon pushes electrons towards nitrogen. Therefore, the pair of electron on nitrogen is relatively more available in methyl amine than in ammonia.

(ii) Stability of cations

The methyl ammonium ion, $\text{CH}_3\text{-NH}_3^+$ is stabilized due to electron donating inductive effect of the methyl group. On the other hand, NH_4^+ ion is not stabilized by hydrogen atoms.

Both these factors favor methylamine to a stronger base than ammonia.



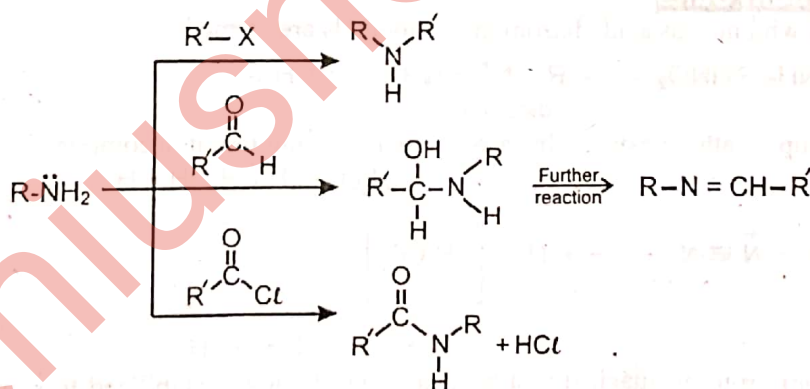
Exception:

Higher members show deviation to these arguments. It is because:

- The stabilization of a positive ion also depends upon the extent of solvation, hydrogen bonding and resonance stabilization.
- The availability of non-bonding pair of electrons is also affected by steric factor in addition to these aspects.

Reactions of Amines

Overview



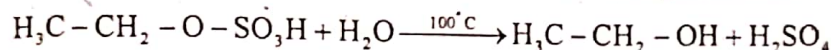
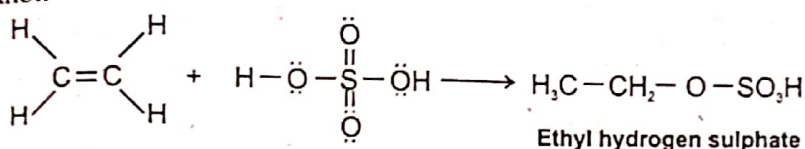
The important organic reactions of amines (nucleophiles) are with the common electrophiles:

- Alkyl halides via nucleophilic substitution
- Aldehydes or ketones via Nucleophilic addition
- Carboxylic acid derivatives, especially acid chlorides or anhydrides, via nucleophilic acyl substitution.

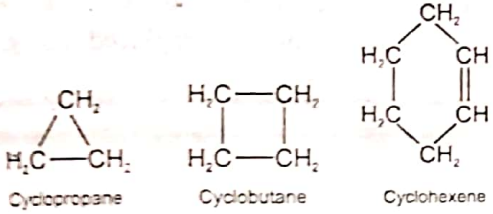
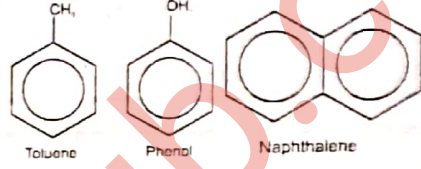
(i) Alkylation of amine by alkyl halides

The alkylation of amine produces sec- or tertiary amines.

form ethanol.



2. What is the difference between alicyclic and aromatic compounds?

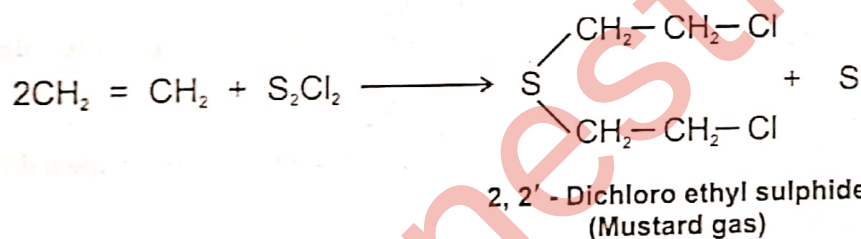
Alicyclic Compounds	Aromatic Compounds
<ul style="list-style-type: none"> The homocyclic compounds which contain ring of three or more carbon atoms and resembling the aliphatic compounds are called alicyclic compounds. They may be saturated or unsaturated. They have low percentage of carbon. 	<ul style="list-style-type: none"> The homocyclic compounds which contain at least one benzene ring are called aromatic compounds. They may contain one or more benzene rings. They have high percentage of carbon.
Examples:  <p style="text-align: center;">Cyclopropane Cyclobutane Cyclohexene</p>	Examples:  <p style="text-align: center;">Toluene Phenol Naphthalene</p>

3. Define IUPAC.

Ans. IUPAC stands for International Union of Pure and Applied Chemistry.

4. Write the equation for the preparation of mustard gas.

Ans.



- The name comes from its mustard like odour.
- It is not a gas, but a high boiling liquid that is dispersed as a mist of tiny droplets.
- It is a powerful vesicant i.e., causes blisters.

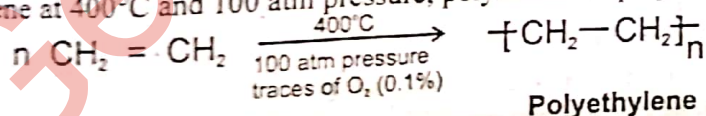
5. Define polymers.

Ans. A large size molecule build up by the repetition of small and simple chemical units (monomers) is called polymer. e.g. polythene, polyester, nylon 6,6 etc.

6. What is polymerization?

Ans. The process in which small organic molecules (monomers) combine together to form larger molecules (polymers) is called polymerization.

e.g. Ethene at 400°C and 100 atm pressure, polymerize to polythene or polyethylene.

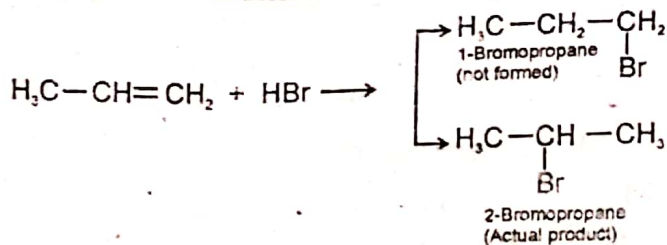


7. What is Markownikov's rule?

Ans. Markownikov's Rule

The addition of hydrogen halide over an unsymmetrical alkene is done by Markownikov's Rule. The rule states that:

"In the addition of an unsymmetrical reagent to an unsymmetrical alkene, the negative part of the adding reagent goes to that carbon, constituting the double bond, which has least number of hydrogen atoms."



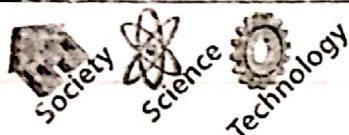
8. What are amines?

Ans. Amines are organic derivatives of ammonia, in which one, two, or all three of the hydrogen atoms of ammonia are replaced by organic groups.

E.g. Compounds RNH_2 are called primary amines, R_2NH secondary amines, and R_3N are tertiary amines.

9. Why halogen of vinyl chloride is inert?

Ans. The reason for this is that the $\text{C}-\text{Cl}$ bond in vinyl chloride ($\text{CH}_2=\text{HC}-\text{Cl}$) is stronger than the $\text{C}-\text{Cl}$ bond in an alkyl chloride ($\text{CH}_3-\text{H}_2\text{C}-\text{Cl}$). This is so because a p orbital on chlorine interacts with the p orbital on the adjacent carbon atom. The new delocalized orbital gives partial double bond character to the $\text{C}-\text{Cl}$ bond in vinyl chloride. As a result the chlorine atom becomes firmly bound to carbon and cannot be replaced easily. However, the carbon-carbon double bond of vinyl chloride shows the usual addition reactions.



ORGANOMETALLIC COMPOUNDS IN MEDICINES

- Cisplatin (C_2H_4)₂ TiCl_2 displays anti-cancer activity in chemotherapy.
- Arene and cyclopentadienyl complexes are kinetically inert platforms for the design of new radiopharmaceuticals.
- Mercurochrome (Merbromin) is an over-the-counter topical antiseptic.
- Merthiolate (Thiomersal) has applications as an antifungal and antiseptic agent. This compound is also used as a vaccine preservative, in immunoglobulin preparations and nasal products.
- Salvarsan (arsphenamine in the States) is an antisyphilis medication.
- Titanocene dichloride, Cp_2TiCl_2 has shown significant anticancer attributes.
- Tamoxifen is an anticancer compound.
- Ferrocenyl derivative chloroquine is an antimalarial compound.
- Titanocene dichloride, $(\text{Cp})_2\text{V}(\text{NCSe})_2$ 1, and carboplatin are anticancer drugs.
- Ferroquine, a combination of ferrocene and chloroquine, is antimalarial drug.
- Vanadocene acetylacetonate has potential in preventing HIV transmission.
- $\text{Ru}(\eta_6\text{-C}_6\text{H}_6)\text{Cl}_2(\text{DMSO})$ has been shown to inhibit topoisomerase II, an important target in chemotherapy.



Do You Know?

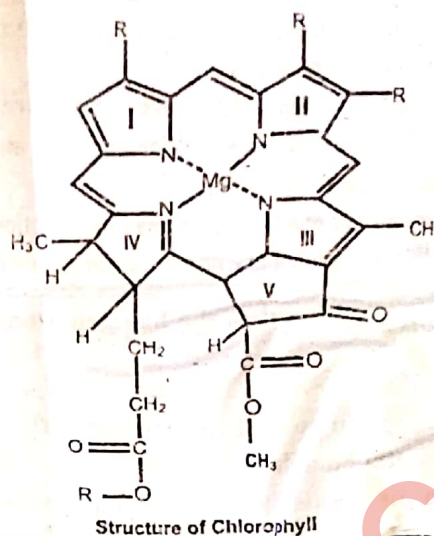
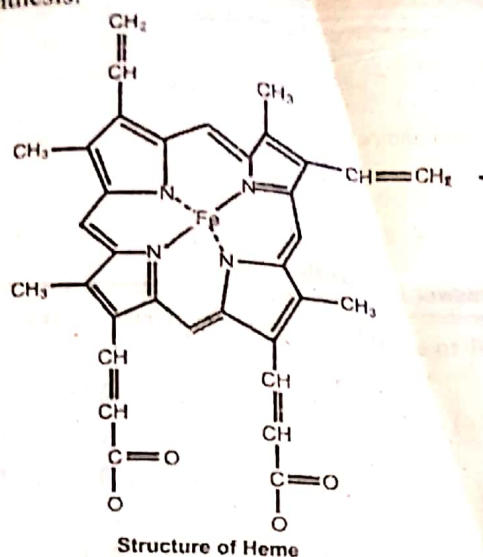
1. CD's are made from vinyl chloride
2. Ethyl chloride is used as a typical anesthetic
3. Erupting volcanoes emit large quantities of halogens and halides.

Comparison between hemoglobin and chlorophyll

Haemoglobin and chlorophyll both are natural organo-metallic compounds. Both consist of a substituted porphyrin ring coordinated with a metal ion.

1. Hemoglobin is a porphyrin ring with iron while chlorophyll is a porphyrin ring with magnesium.
2. Hemoglobin is the red pigment in the blood while chlorophyll is the green pigments in green plants, algae, and certain organisms.

3. Hemoglobin is involved in oxygen transport while chlorophyll functions as a receptor of light energy during photosynthesis.



KEY POINTS

- Monohalo derivatives of alkanes are called alkyl halides.
- The general formula of alkyl halides is $C_nH_{2n+1}X$.
- The best method for the preparation of alkyl halides is by the reactions of alcohols with inorganic halides like $SOCl_2$, PX_3 and PX_5 .
- Alkyl halides are very reactive class of organic compounds. They undergo nucleophilic substitution reactions and elimination reaction in the presence of nucleophile or a base.
- Nucleophilic substitution reactions can take place in two distinct ways. A one step mechanism is called S_N2 while a two-step mechanism is called S_N1 . S_N1 reaction show first order kinetics whereas S_N2 reaction show 2nd order kinetic.
- Nucleophilic substitution reactions take place simultaneously with elimination reaction and often compete with them.
- Elimination of two atoms or groups from adjacent carbon atoms in the presence of a nucleophile or a base is called elimination reaction. Like nucleophilic substitution, β -elimination reactions also take place in two distinct ways E2 and E1.
- A nucleophile is an the electron rich species that will react with an electron poor species
- A substitution implies that one group replaces another.
- Grignard reagent can be prepared by adding alkyl halide in a stirred suspension of magnesium metal in diethyl ether.
- Grignard reagent has a reactive nucleophilic carbon atom which can react with electrophilic centered to give the products in high yields. Primary, secondary and tertiary alcohols can be best prepared by reacting Grignard reagent with formaldehyde, any other aldehydes and ketones, respectively.
- The polar nature of the N - H bond (due to the electronegativity difference of the two atoms) results in the formation of hydrogen bonds with other amine molecules.
- Primary amines, $R-NH_2$ or $ArNH_2$, undergo nucleophilic addition with aldehydes or ketones to give carbinolamines which then dehydrate to give substituted imines.
- Primary alkyl or aryl amines yield diazonium salts.

11. Multiple Choice Questions. Encircle the correct answer:

- ⊛ Read the question carefully.
- ⊛ Try to answer the question yourself before reading the answer choices.
- ⊛ Guess only if you can eliminate one or more answer choices.
- ⊛ Drawing a picture can help.
- ⊛ Don't spend too much time on any one question.
- ⊛ In-depth calculations are not necessary; approximate the answer by rounding.

- i) In primary alkyl halides, the halogen atom is attached to a carbon which is further attached to how many carbon atoms;
(a) two (b) three (c) one (d) four
- ii) S_N2 reactions can be best carried out with:
(a) primary alkyl halides (b) secondary alkyl halides (c) tertiary alkyl halides (d) all the three
- iii) For which mechanisms, the first step involved is the same;
(a) $E1$ and $E2$ (b) $E2$ and S_N2 (c) $E1$ and S_N2 (d) $E1$ and S_N1
- iv) The rate of $E1$ reaction depends upon;
(a) the concentration of substrate (b) the concentration of nucleophile.
(c) the concentration of substrate as well as nucleophile (d) none of the above.
- v) Alkyl halides are considered to be very reactive compounds towards nucleophiles, because:
(a) they have an electrophilic carbon
(b) they have an electrophilic carbon and a good leaving group
(c) they have an electrophilic carbon and a bad leaving group
(d) they have a nucleophilic carbon and a good leaving group
- vi) Which one of the following is not a nucleophile?
(a) H_2O (b) H_2S (c) BF_3 (d) NH_3
- vii) Double bond is formed as a result of;
(a) substitution reactions (b) elimination reactions (c) addition reactions (d) rearrangement reactions
- viii) Which of the following alkyl halides cannot be formed by direct reaction of alkanes with halogen?
(a) RBr (b) RCl (c) RF (d) RI
- (ix) $CH_3CH_2CH_2Br$ on treatment with alc KOH gives:
(a) propanal (b) propene (c) propane (d) none
- (x) Grignard's reagent gives alkane with;
(a) water (b) ethylamine (c) ethanol (d) all of these
- (xi) Action of alkyl halides with Na metal yield;
(a) alkanes (b) alcohols (c) alkenes (d) phenols
- (xii) Alkyl halides react with excess of ammonia to give;
(a) 1° -amine (b) 2° -amine (c) 3° -amine (d) all
- (xiii) Among the alkyl halides the primary alkyl halides always follow the mechanism;
(a) S_N1 (b) S_N2 (c) S_N3 (d) S_N4
- (xiv) Grignard's reagent on treatment with chloramines gives;
(a) acetamide (b) primary amine (c) secondary amine (d) urea
- (xv) Nucleophilic addition of a primary amine giving;
(a) imine (b) urea (c) ammonia (d) nitrobenzene

SOLVED EXERCISE MCQs

Q. No	Answer	Reason
(i)	(c) one	Primary alkyl halides are those in which halogen atom is attached with a carbon atom which is further attached to one or no carbon atom. e.g: $\text{CH}_3 - \text{Cl}$ $\text{CH}_3 - \text{CH}_2 - \text{Cl}$ $\text{CH}_3 - \text{CH}_2 - \text{CH}_2 - \text{Cl}$ Chloromethane Chloroethane 1-Chloropropane
(ii)	(a) primary alkyl halides	Because steric hindrance in Primary alkyl halides is less and primary carbocation is unstable.
(iii)	(d) E1 and S _N 1	In both mechanisms, first step is ionization of tertiary alkyl halide.
(iv)	(a) the concentration of substrate	First step is rate determining step in which reactant is substrate.
(v)	(b) they have an electrophilic carbon and a good leaving group	$\text{Nu} + \begin{array}{c} \\ \text{---C---} \\ \end{array} \text{---L} \longrightarrow \text{Nu---C---} + \text{L}^-$
(vi)	(c) BF ₃	BF ₃ has no electron pair or negative charge on central atom 'B'. So it attracts electrons and acts as electrophile.
(vii)	(b) elimination reactions	$\begin{array}{c} \text{H}_2\text{C} - \text{CH}_2 \\ \quad \\ \text{H} \quad \text{Br} \end{array} + \text{KOH} \xrightarrow{\text{Alcohol}} \text{H}_2\text{C} = \text{CH}_2 + \text{KBr} + \text{H}_2\text{O}$ <p style="text-align: center;">Ethene</p>
(viii)	(d) RI	Alkyl iodides cannot be prepared by the direct iodination of alkanes. An excellent method for the preparation of simple alkyl iodide is the treatment of alkyl chloride or alkyl bromide with sodium iodide. $\text{RCl} + \text{NaI} \longrightarrow \text{RI} + \text{NaCl}$ $\text{RBr} + \text{NaI} \longrightarrow \text{RI} + \text{NaBr}$
(ix)	(b) propene	$\text{CH}_3 - \text{CH}_2 - \text{CH}_2 - \text{Br} + \text{KOH} \xrightarrow{\text{alcohol}} \text{CH}_3 - \text{CH}_2 - \text{CH} = \text{CH}_2 + \text{KBr} + \text{H}_2\text{O}$
(x)	(d) all of these	$\begin{array}{c} \delta^- \quad \delta^+ \quad \delta^- \quad \delta^+ \\ \text{CH}_3 - \text{CH}_2 - \text{Mg} - \text{Br} + \text{H} - \overset{\delta^-}{\text{O}} - \overset{\delta^+}{\text{H}} \\ \text{Ethylmagnesium bromide} \quad \text{Water} \end{array} \xrightarrow{\text{Ether}} \begin{array}{c} \text{CH}_3 - \text{CH}_3 + \text{Mg} \begin{array}{l} \text{Br} \\ \text{OH} \end{array} \\ \text{Ethane} \end{array}$ $\begin{array}{c} \delta^- \quad \delta^+ \quad \delta^- \quad \delta^+ \\ \text{CH}_3 - \text{CH}_2 - \text{Mg} - \text{Br} + \text{CH}_3 - \text{CH}_2 - \overset{\delta^-}{\text{O}} - \overset{\delta^+}{\text{H}} \\ \text{Ethylmagnesium bromide} \quad \text{Ethanol} \end{array} \xrightarrow{\text{Ether}} \begin{array}{c} \text{CH}_3 - \text{CH}_3 + \text{Mg} \begin{array}{l} \text{Br} \\ \text{OCH}_2\text{CH}_3 \end{array} \\ \text{Ethane} \end{array}$
(xi)	(a) alkanes	Alkyl halides react with sodium in dry ether solvent to give alkanes. The reaction is particularly useful for the preparation of symmetrical alkanes. $\text{CH}_3 - \text{CH}_2 - \text{Cl} + 2\text{Na} + \text{Cl} - \text{CH}_2 - \text{CH}_3 \xrightarrow{\text{Ether}} \text{CH}_3 - \text{CH}_2 - \text{CH}_2 - \text{CH}_3 + 2\text{NaCl}$ <p style="text-align: center;">n - Butane</p>
(xii)	(d) All	$\begin{array}{c} \delta^+ \quad \delta^- \\ \text{CH}_3 - \text{CH}_2 - \text{Br} \end{array} + \text{H}_3\text{N} \longrightarrow \text{C}_2\text{H}_5 - \text{NH}_2 + \text{HBr}$ <p style="text-align: center;">Ethylamine</p> $\begin{array}{c} \delta^+ \quad \delta^- \\ \text{CH}_3 - \text{CH}_2 - \text{Br} \end{array} + \text{CH}_3 - \text{CH}_2 - \text{NH}_2 \longrightarrow (\text{CH}_3 - \text{CH}_2)_2\text{NH} + \text{HBr}$ <p style="text-align: center;">Diethylamine</p> $\begin{array}{c} \delta^+ \quad \delta^- \\ \text{CH}_3 - \text{CH}_2 - \text{Br} \end{array} + (\text{CH}_3 - \text{CH}_2)_2\text{NH} \longrightarrow (\text{CH}_3 - \text{CH}_2)_3\text{N} + \text{HBr}$ <p style="text-align: center;">Triethylamine</p>

(xiii)	(b) S_N2	Because steric hindrance in Primary alkyl halides is less and primary carbocation is unstable.
(xiv)	(b) primary amine	The reaction is: $CH_3MgCl + NH_2Cl \longrightarrow CH_3NH_2 + MgCl_2$
(xv)	(a) imine	Nucleophilic addition of amine to carbonyl compounds give imine.

SHORT ANSWERS QUESTIONS

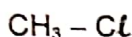
2. Give brief answers for the following questions.

(i) What are primary, secondary and tertiary alkyl halides?

Ans. (i) Primary Alkyl Halides:

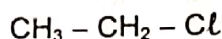
"Alkyl halides in which halogen atom is attached with primary carbon are called primary alkyl halide".

Examples:



Methyl chloride

(Chloromethane)



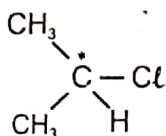
Ethyl chloride

(Chloroethane)

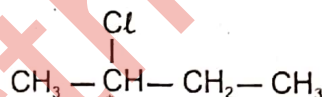
(ii) Secondary Alkyl Halides:

"Alkyl halides in which halogen atom is attached with a secondary carbon atom are called secondary alkyl halides."

Examples:



Iso-Propyl chloride or
2-Chloropropane

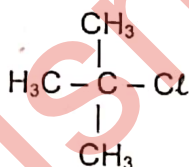


Sec-Butyl chloride or
2-Chlorobutane

(iii) Tertiary Alkyl Halides:

"Alkyl halides in which halogen atom is attached to a tertiary carbon are called tertiary alkyl halide".

Example:



t-Butyl chloride
(2-Methyl-2-chloropropane)

(ii) Why alkyl iodides cannot be prepared by directly heating iodine with alkene?

Ans. Direct reaction of hydrocarbon with iodine is:

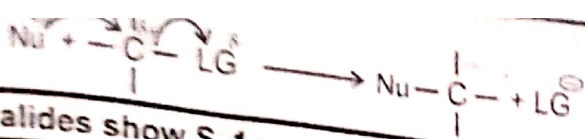
(i) Thermodynamically not favorable.

(ii) Reversible because 1,2- di-iodoalkane product is unstable.

(iii) HI formed which is reducing agent. Hence the reaction must be carried in the presence of oxidization agent like HNO_3 to neutralize the HI formed.

(iii) What are Nucleophilic substitution reactions or S_N reaction?

Ans. Those reactions in which the halogen is replaced by some other atom or a group are called nucleophilic substitution, or S_N reactions.



(v) Tertiary alkyl halides show S_N1 reactions mostly, why?

Ans. Due to following factors tertiary alkyl halides show S_N1 reaction:

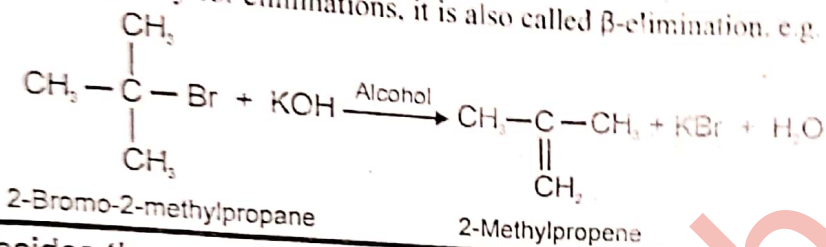
- Stability of carbocation
- Steric hindrance due to bulky groups
- Weak electrophilic nature of α -carbon

(vi) What are elimination reactions?

Ans. Elimination Reactions:

"The chemical reactions in which two groups are eliminated from two adjacent atoms are called elimination reactions."

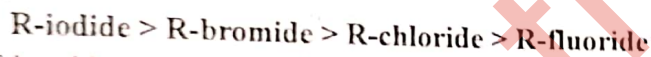
Since β -hydrogen is necessary for eliminations, it is also called β -elimination, e.g.



(vii) Which factor decides the reactivity of alkyl halides?

Ans. Experiments have shown that the bond energy of C-X bond is the main factor which decides the reactivity of alkyl halides, and not the polarity of the molecule.

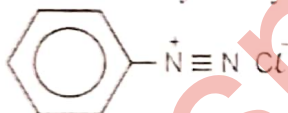
A study of bond energies of C-X bond shows that C-F bond is the strongest. So the overall order of reactivity of alkyl halides is:



In fact the C-F bond is so strong that alkyl fluorides do not react under ordinary conditions.

(viii) What are the diazonium salt?

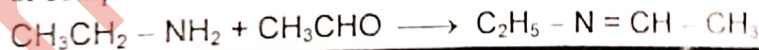
Ans. Diazonium salts are a group of organic compounds sharing a common functional group $\text{R}-\text{N}_2^+ \text{X}^-$ where R can be any organic residue such as alkyl or aryl and X is an inorganic or organic anion such as a halogen.



Benzenediazonium chloride

(ix) How can nucleophilic addition of a primary amine giving an imine?

Ans. The electrophilic carbon atoms of aldehydes and ketones can be targets of nucleophilic attack by primary amines. The end result of this reaction is a compound in which the C=O double bond is replaced by a C=N double bond. This type of compound is known as an imine, or Schiff base.



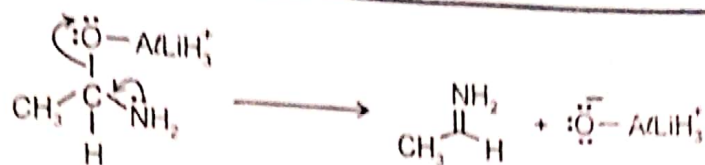
(x) Amines are more basic than analogous alcohols. Why?

Ans. Amines are more basic than analogous alcohols due to following reasons:

- The lone pair of electrons on nitrogen is more available for proton (H^+) than lone pair of oxygen.
- The electronegativity of 'N' is less than that of 'O'.
- $\text{R}-\text{NH}_3^+$ is more stable than $\text{R}-\text{O}^+\text{H}_2$.

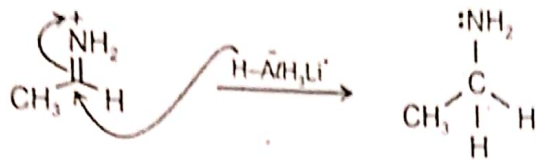
(xi) How tertiary alcohols are obtained from R-Mg-X?

Ans. Tertiary alcohols are obtained when Grignard's reagents react with ketones e.g.



Step 3:

Rapid reduction by the nucleophilic H from the hydride reagent as it adds to the electrophilic C in the iminium system. π electrons from the C=N move to the cationic N neutralizing the charge creating the amine product.



Skill Activity

Take a piece of Iron metal and put it in open air and note the colour of rust, in which process this rust will make.



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