CHAPTER 17

ALKYL HALIDES AND AMINES

After completing this lesson, you will be able to:

- name alkyl halides using IUPAC system.
- Discuss the and reactivity of RX.
- Describe the preparation of RX by the reaction of alcohols with WC, SQC12 and by radical halogenations of alkanes.
- Describe the mechanism and types of nucleophilic substitution reaction (Understanding)
- Describe the and types of elimination reactions.
- Describe the preparation and reactivity of GriB1ard's' Reagents.
- Discuss chemistry of Grignard's reagent by the addition of aldehyde, ketones, ester and carbon dioxide.
- Discuss and basicity of amines. Describe the preparation amines by alkylation of ammonia to RX and reduction of nitriles, nitro and functional groups.
- Discuss reactivity of amines.
- Describe chemistry of amines by alkylation of amines wit RX, reaction with ketones preparations of amides and diazonium salts.

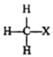
QI. What are alkyl Halides? Explain with examples.

Answer

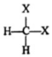
"Alkyl halides are the compounds in which one hydrogen atom of Alkanes has been replaced by one halogen atom. They are also known as halogen derivatives."

Types:

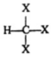
They may be Mono, di, tri or poly haloalkanes depending upon the number of halogen atoms present in the molecule. Monohaloalkanes are called alkyl halides having general formula R-X.



Monohaloalkane



Dihaloalkane



Trihaloalkane

Classification of Alkyl Halides:

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

i) **Primary Alkyl Halides:** [redacted]

"Alkyl halide in which halogen atom is attached with primary carbon are called primary halides. Carbon atom attached to one or no carbon atom is called primary C - atom."

$\dot{C}H_3-Cl$ methyl chloride chloromethane

$CH_3-\dot{C}H_2-Cl$ Ethyl chloride chloromethane

$CH_3-CH_2-\dot{C}H_2-Cl$ n-propyl chloride chloropropane

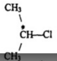
($\dot{C}$ is a primary carbon atom)

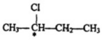
ii) **Secondary Alkyl Halides:**

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

Secondary C-atom:

"C-atom, attached to two C-atoms simultaneously is called secondary C-atom."





$CH_3-\underset{\bullet}{\overset{Cl}{\overset{|}{C}H}}-CH_2-CH_3$

Iso-Propyl chloride 2-Chloro propane

Sec-Butyl chloride 2-Chlorobutane.

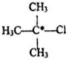
($\dot{C}$ is the secondary carbon atom)

iii) Tertiary Alkyl Halides:

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

Tertiary C-atom

"C-atom, attached to three C-atoms simultaneously is called tertiary C-atom".



$H_3C-\dot{C}(CH_3)_2-Cl$

t- Butyl chloride
2-Methyl-2-chloropropane.

($\dot{C}$ is tertiary carbon atom)

Nomenclature of Alkyl halides

Alkyl halides are named according to the following systems:

i) Common System of naming.

ii) IUPAC System of naming.

I) Common System of Naming:

This method consists in first writing the name of alkyl group to which halogen atom is attached and then writing the name of halide ion, e.g.,

$CH_3\_CH_2\_Cl$	Ethyl Chloride

For secondary alkyl halides, the prefix sec _ and for tertiary alkyl halides, the prefix ter_ to t_ is added before the name of alkyl halides, e.g,.

CH_2 _ CH _ Br   Sec or isopropyl Bromine
|
CH_3

CH_3
|
CH_3_ CH _ Br   ter_ butyl bromide
|
CH_3

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,

$CH_3\_CH_2\_CH_2\_CH_2\_Br$	n-butyl bromide

II) IUPAC System of naming.

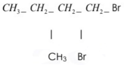
According to this system alkyl halides are named as derivatives of alkanes. The following rules are observed for this purpose:

i) The longest chain bearing halogen is selected as parent hydrocarbon.

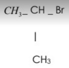
ii) Prefix 'halo' i.e., chloro for Cl, Bromo for Br, etc, is used before the name of hydrocarbon.

iii) Positional numbers are used to indicate halogen and other substituent by the usual methods,

$CH_3-CH_2-CH_2-CH_2-Br$ **bromo butane**


$CH_3-\underset{\underset{CH_3}{|}}{CH_2}-\underset{\underset{Br}{|}}{CH_2}-CH_2-Br$

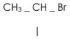
2 – bromo_ 3 _ methyl butane


$CH_3-\underset{\underset{CH_3}{|}}{CH}-Br$

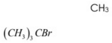
2 - bromo propane

The names given below are also accepted by the IUPAC

CH_3-CH_2-Cl **Ethyl Chloride**


$CH_3-\underset{|}{CH}-Br$

iso _ propyl Bromide


CH_3

$(CH_3)_3CBr$

ter_butyl bromide

Q2. Give Physical Properties of Alkyl Halides

Answer

I) 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 a s bond.
- The carbon halogen is typically quite polar due to the electronegativity and polarizability of the halogen.

Q3. Give preparations of alkyl halides.

Answer

1) Reaction of Alcohols with Hydrogen Halides

Alcohols may be converted to the corresponding alkyl halides by the action of halogen acid in the presence of ZnC12, which acts as a catalyst.

$ZnCl_2$

$$CH_3CH_2 - OH + HX \longrightarrow CH_3CH_2 - X + H_2O$$

2) Reaction of Alcohols with other Halogenating agents (SOCla, PX,)

a) Alcohols reacts with thionyl chloride in pyridine as a solvent to give alkyl chlorides.

This is the best method because HCl, and S02 escape leaving behind the pure product.

$$ROH + SOCL_2 \rightarrow R\text{-}Cl + SO_2 + HCl$$

b) Phosphorous or phosphorous pentahalides react with alcohols to from alky halides.

$$3CH_3\text{-}CH_2\text{-}OH + PBr_3 \rightarrow 3CH_3\text{-}CH_2\text{-}Br + H3PO_3$$

$$CH_3\text{-}CH_2\text{-}OH + PCl_5 \rightarrow CHECH_2\text{-}Cl + POCl_3 + HCl$$

3) Halogenation of Alkanes

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

$$CH_3.CH_3 + C1_2 \rightarrow CH_3.CH_2Cl + HCl$$

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

The detail mechanism of this reaction has already been discussed in section 16.3.2.

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

1) Bond Polarity

The molecule of alkyl halide is polarized due to the greater electronegativity of halogens as compared to C.

Atom	Electronegativity	Atom	Electronegativity
F	4.0	I	2.5
Cl	3.0	H	2.1
Br	2.8	C	2.5

Hence carbon acquires partial positive whereas halogens acquires partial negative charge. Halogen becomes nucleophilic in character, which can be replaced by another nucleophile.

2) Bond Energy

Experiments have shown that the bond energy of C-X bond is the main factor which decides the reactivity of alky 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:

R-iodide > R-bromide > R-chloride > R-fluoride

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

Q4. Give nucleophilic substitution reactions of alkyl halides.

Answer

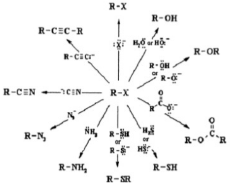
1) Alkyl chlorides, bromides and iodides are good substrates for substitution reactions.

2) A variety of nucleophiles can be used to generate a range of new functional groups.

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

4) For practice, make sure you can draw the mechanisms that lead to these products.

Reactions

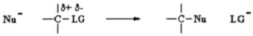


Nucleophilic Substitution Reactions

General Introduction What does the term nucleophilic substitution imply?

- **A nucleophile** is electron rich species that will react with an electron poor species
- **A substitution** implies that one group replaces another.

Nucleophilic substitution reactions occur when an rich species, the nucleophile, reacts at an electrophilic C atom attached to an electronegative group (important), the leaving group, that can be displaced as shown by the general scheme:



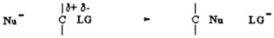
$$Nu^- \quad -\overset{|\ \delta+\ \delta-}{\underset{|}{C}}-LG \longrightarrow -\overset{|}{\underset{|}{C}}-Nu \quad LG^-$$

The electrophilic C can be recognized by looking for the polar sigma bond due to the presence of an electronegative substituent (esp. C-Cl, C-Br, C-I and C-O)

Nucleophilic substitution reactions are an important class of reactions that allow the interconversion of functional groups.

Of particular importance are the reactions of alkyl halides (R-X) and alcohols (R-OH) For alcohols, the range of substitution reactions possible can be increased by utilizing the tosylates (R-OTs), an alternative method of converting the -OH to a better leaving group.

Overall a nucleophilic substitution can be represented as follows:



$$Nu^- \quad \overset{\delta+}{C}\;\overset{\delta-}{LG} \rightarrow C\;Nu \quad LG^-$$

There are two fundamental events in a nucleophilic substitution reaction:

I) formation of the new s bond to the nucleophile

2) breaking of the s bond to the leaving group

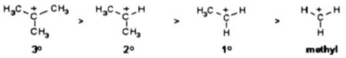
Depending on the relative timing of these events, two different mechanisms are possible:

- Bond breaking to form a carbocation precedes the formation of the new bond: SNI reaction
- Simultaneous bond formation and bond breaking: SN2 reaction

CARBOCATIONS AND THEIR STABILITY

Stability:

The general stability order of simple alkyl carbocations is: (most stable) $3^0 > 2^0 > 1^0$ > 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

I) Substitutions via the SNI

2) Eliminations via the El

3) Additions to alkenes and alkynes (HX, H30+)

Q5. Define nucleophiles and Base.

Answer

It is species rich in electron and has an unshared pair of electrons available for bonding. In most cases it is basic. It may be negatively charged or neutral.

Examples of Nucleophiles:

OH^- Hydroxide ion

NH_2^- Amino group

$C_2H_5O^-$ Ethoxide ion

Cl^- chloride ion

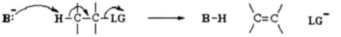
HS^- hydrogen sulphide ion

Br^- bromide ion

SCN^- thio cynate ion

$\ddot{N}H_3$ ammonia

$H_2\ddot{O}:$ water


E2

Q6. Define substrate and leaving group.

Answer

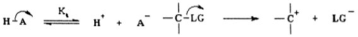
Substrate Molecule:

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, Cl-, Br-, I- HS04- are good leaving groups. Poor leaving groups are OH-, OR and NH2-, Iodide ion is a good nucleophile as well as a good leaving group.

What do we mean by this? First, we should write the chemical equations for the two processes:



These two equations represent Bronsted acid dissociation and loss of a leaving group in a SNI type reaction. Note the similarity of the two equations: both show heterolytic cleavage of a s bond to create an anion and a cation.

For acidity, the more stable A is, then the more the equilibrium will favor dissociation, and release of protons meaning that HA is more acidic.

For the leaving group, the more stable LG- is, the more it favors "leaving".

Hence factors that stabilize A- also apply to the stabilization of a LG-.

Type equation here.Here is a table classifying some common leaving groups that we will eventually meet Excellent

Excellent	TsO, NH3
Very Good	T, H2O
Good	Br
Fair	Cl
Poor	F
Very Poor	Ho, NH2, RO

But water itself, H20, is a good leaving group, since it is the conjugate base of H30+ which

Q7. Give SNI Reaction mechanism.

Answer

SN, Mechanism

"It is substitution nucleophilic unimolecular two step reaction."

Explanation:

The substrate R-X first ionizes reversibly into R= and X- ions.

$$R-X \overset{SLOW}{\rightleftharpoons} R^{+}+X^{-}$$

Then the carbonium ion combines with the attacking nucleophile to form product.

$$R^{+}+\bar{Nu} \xrightarrow{fast} R-Nu$$

Since only one molecule is undergoing a change in covalency in rate determining step, this two-step nucleophilic substitution reaction is unimolecular and is called SNI reaction. The brief mechanistic picture of SNI reaction based upon the following evidences:

1) **Kinetic Evidence:**

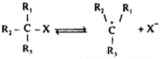
The rate of an SNI reaction depends upon the concentration of alky halide only. The change is concentration of attacking nucleophile has no effect on the rate

Rate = k[R- X]

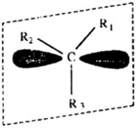
It is because the nucleophile combines with the carbonium ion in the second sep. for the same reason, the rate of an SNI reaction does not depend on the nature of attacking nucleophile.

2) **Stereo Chemical Evidence:**

Experiments have shown that SNI reaction occur with partial racemization. The extent of partial racemization depends upon several factors including stability f carbonium ion.

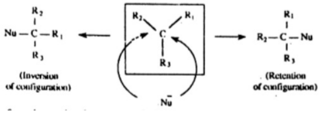


(Carbonium ion)



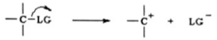
The carbon atom of carbonium ion is sp2 hybridized and carries one empty p-orbital. The nucleophile can attach itself to the p-orbital either on the right or on the left side of carbon with equal ease. The expected product is a recemic mixture. However, the partial recemization suggests a different way of attachment, e.g., in case of unstable carbonium ion, 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

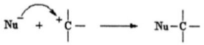


Therefore, the product has some optical activity.

Step1: slow loss of the leaving group, to generate a carbocation intermediate



Step2: rapid attack of a nucleophile on the electrophilic carbocation to form a new s bond



Q8. Give SN2 Reaction Mechanism.

Answer

"It is substitution nucleophilic bimolecular reaction. It occurs in one step".

Explanation:

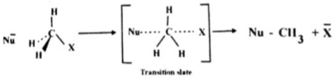
Consider the reaction:

$$N\bar{u} + CH_3 - X \rightarrow Nu - CH_3 + \overline{X}$$

(Nucleophile)

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.

1) **Kinetic Evidence:**

The rate of an SN2 reaction depends upon the concentration of nucleophile as well as the concentration of alky halide. The ate expression for the reaction

$$N\bar{u} + R - X \rightarrow Nu - R + \bar{X}$$

can be written as

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

Where k = specific rate constant.

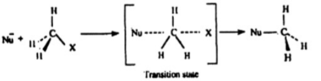
This means that the rate of reaction will be double if the concentration of any of the two is double e.g., the rate of hydrogen.

CH_2- Br + $\bar{O}$H → CH_3 - OH + Br

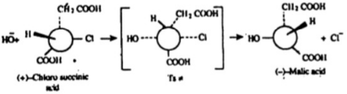
Increases when either OH or CH3-Br is increased.

2) Stereo Chemical Evidence:

A bimolecular nucleophilic substitution always occurs with inversion of configuration. The carbon atom in transition state is sp²-hybridized and is planar. The attacking nucleophile ad the leaving groups are present in the transition state on opposite sides of electrophilic carbon atom.



In methyl chloride, we cannot prove the inversion of configuration because it is optically inactive. However, the reaction of a hydroxide ion with chloro succinic acid is found to occur with inversion of configuration.



Comparison of SNI and SN2 Mechanism

Sr. No.	SNI	Sr.	SN2
(I)	It is a two step mechanism.	(I)	It is a single step mechanism.
(2)	First step is slow one and second is fast.	(2)	It has only one step and that is slow.
(3)	It is a unimolecular reaction.	(3)	It is a bimolecular reaction.
(4)	It is favoured in polar solvents.	(4)	It is favoured in non-polar solvents.
(5)	Mostly tertiary alkyl halides give this reaction.	(5)	Mostly primary alkyl halides give this reaction.
(6)	50 % is inversion and 50% retension of configuration takes place.	(6)	100% inversion of configuration takes place.

Q9. What are Elimination Reactions?

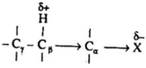
Answer

Definition of Elimination Reaction:

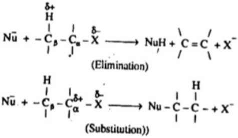
"The chemical reaction in which two groups are eliminated from two adjacent atoms is called elimination reaction". Since ß-hydrogen is necessary for eliminations, it is also called P-elimination.

Explanation:

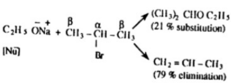
P-hydrogen atom in alkyl halides is slightly acidic due to electron with drawing effect of halogen.



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



Strong bases such as OH, OR, NH2 cause elimination in preferences to substitution. Highly polarizable nucleophile and weak bases such as r, RS- etc. give substitution reactions.

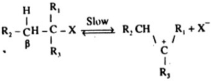

$C_2H_5\overset{-}{O}\overset{+}{Na} + \overset{\beta}{CH_3}-\overset{\alpha}{CH}(Br)-\overset{\beta}{CH_3}$
(Nū)
$(CH_3)_2CHOC_2H_5$
(21 % substitution)
$CH_2=CH-CH_3$
(79 % elimination)

El Mechanism

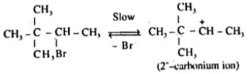
"It is unimolecular two step elimination reactions."

Explanation:

The substrate undergoes slows ionization in the first step to form carbonium ion,



In the second step the solvent or base pulls off a P-hydrogen

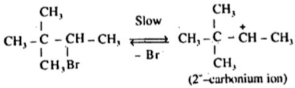


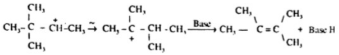
Since only one molecule is undergoing a change in the rate determining step, i.e., first step, this is two step unimolecular elimination reactions.

The El-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.

Rate = k[R-X1

The presence of carbonium ion as an intermediate has been indicated by the presence of more than of kind of elimination products. A relatively less stable carbonium ion rearranges to give stabler carbonium before giving elimination product.



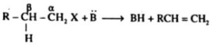


E2 mechanism

"It is bimolecular one step elimination reaction".

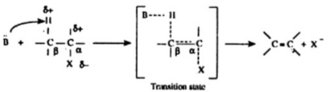
Explanation:

Consider the reaction,



$$R-\overset{\beta}{\underset{\substack{|\\H}}{C}}H-\overset{\alpha}{C}H_2X+\ddot{B}\longrightarrow BH+RCH=CH_2$$

The attacking base removes a proton from the ß-carbon simultaneously with the formation of double bond between Ca and Cp and the loss of halide ions.

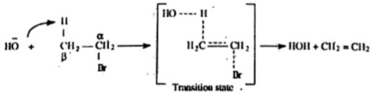


This is rate determining step because bond breaking and bond making processes are taking place simultaneously.

Since two molecules are undergoing 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. The observed rate law the E2-reaction is

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

The rate of E2-reaction depends upon the concentration of substrate and the base e.g., for the reaction



The rate of reaction follows second order kinetics

$$\text{Rate} = k\ [CH_3,\ CH_2\ Br]\ [OHI$$

Q10. Give a Comparison of Substitution & Elimination Reactions.

Answer

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 more favorable energetically it is the dominant reaction in the substitution-elimination reaction.

Elimination occurs only in the presence of B-H 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 substitute because the approach of the nucleophile to a-carbon is difficult for substitution. However, the elimination is favorable because the removal of B-H atom by base from tertiary planar carbonium ion is easy, e.g.,

$$CH_3-CH_2S(CH_3)_2+C_2H_5\bar{O}Na^+ \xrightarrow{C_2H_5OH} CH_3CH_2OC_2H_5+CH_2=CH_2$$

(elimination =12%)

CH_3

\\

$$CH_3-CH_2S(CH_3)_2+C_2H_5\bar{O}Na^+ \xrightarrow{C_2H_5OH} CH_3CH_2OC_2H_5+CH_2=CH_2$$

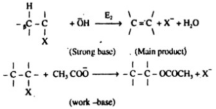
/ |

CH_3 CH_3

Subsl. 39% (elimination = 61%)

ii) Nature of Base:

When the electron pair donor is a strong base, e.g., OH, OR etc., the dominant reaction is E2 and SN2 reaction is a side reaction. However, when the nucleophile is a weak base like X-, RS-, etc,. The main reaction will be substitution and E2 will be minor side reaction.



iii) the nature of Leaving Group:

The role of leaving groups in Elimination reactions is similar to that in substitution reactions. In unimolecular reactions it does not affect the mechanism because both the elimination and substitution products are decided with carbonium ion. However, in the bimolecular reactions the nature of product greatly depends upon the nature of leaving group, e.g.,

$$n-C_{18}H_{37}-X+(CH_3)_3COK \xrightarrow{(CH_3)_3COH} nC_{16}H_{33}CH \equiv CH_2+nC_{18}H_{37}OC(CH_3)_3$$

X=Br 85%

15%

X=OTS 1%

99%

iv) Nature of Solvent

Elimination is favored more than substitution by decreasing the solvent polarity. Thus, alcoholic KOH affects elimination while more polar aqueous KOH is used for substitution. El is favored by polar solvents like Snl reaction. In non-polar solvents, the reaction will follow E2-mechansim.

v) Effect of Temperature

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

$$(CH_3)_3CCl \xrightarrow[Unimolecular]{H_2O} (CH_3)_2C = CH_2 + (CH_3)_3COH$$

at 25°C 17% 83%

at 65°C 36% 64%

$$(CH_3)_3CCl \xrightarrow[Unimolecular]{H_2O} (CH_3)_2C = CH_2 + (CH_3)_3COH$$

|

Br

at 45°C 53%

47%

at 100°C 64%

36%

Q11.What are Organ metallic Compounds (Grignard's Reagents)? Give their preparation & Reactions.

Answer

Preparation of Grignard's Reagents

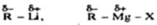
Magnesium metal cut into small pieces is added to a solution in of an alkyl halide or awl halide in only dry ether. The reaction mixture is heated with electric heater in a round bottom flask fitted with condenser and other arrangement to avoid the contact of moisture or oxygen.

$$R - X + Mg \xrightarrow[Ether]{\Delta} R\,Mg\,X$$

Alky bromide are generally used in the preparation Grignard's reagent s 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 of Grignard's Reagent

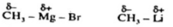
Organo metallic compounds are nucleophile because of partial negative charge on the carbon of alkyl group



$$\overset{\delta-}{R} - \overset{\delta+}{Li}, \qquad \overset{\delta-}{R} - \overset{\delta+}{Mg} - X$$

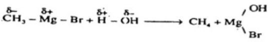
Carbon atom being more electronegative that metals such as Mg, Li etc., thy alkyl

group as a whole bears partial negative charge and organo metallic compounds act as source of nucleophile, e.g.,



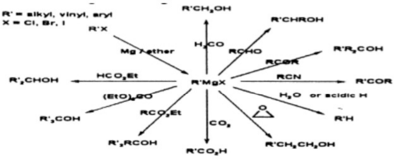
$$\overset{\delta-}{CH_3} - \overset{\delta+}{Mg} - Br \qquad \overset{\delta-}{CH_3} - \overset{\delta+}{Li}$$

The following reaction supports the electrophilic character of organic metallic compounds;



$$\overset{\delta-}{CH_3} - \overset{\delta+}{Mg} - Br + \overset{\delta+}{H} - \overset{\delta-}{OH} \longrightarrow CH_4 + Mg\begin{smallmatrix} OH \\ Br \end{smallmatrix}$$

Reactions of Grignard's Reagents



Typical work-up for these reactions:
1. Dilute aqueous acid or
2. Aqueous ammonium chloride

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 H30+. First two reaction are with aldehydes while third belongs to ketones.

Classification of Monohydric Alcohols:

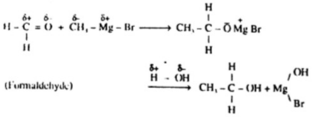
Monohydric alcohols are classified into the following three families:

i) Primary alcohols

ii) Secondary alcohols

iii) Tertiary alcohols

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

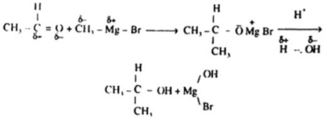


$$H-\underset{H}{\overset{\delta+}{C}}=\overset{\delta-}{O}+\overset{\delta-}{C}H_3-\overset{\delta+}{Mg}-Br \longrightarrow CH_3-\underset{H}{\overset{H}{C}}-\bar{O}\overset{+}{Mg}Br$$

(Formaldehyde)

$$\xrightarrow{\overset{\delta+}{H}-\overset{\delta-}{OH}} CH_3-\underset{H}{\overset{H}{C}}-OH+Mg\begin{matrix}OH\\Br\end{matrix}$$

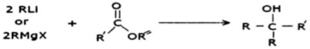
ii) Reaction with Ethanal (Aldehyde) to form secondary alcohol



$$CH_3-\overset{H}{\underset{\delta-}{C}}=\underset{\delta-}{O}+\overset{\delta-}{C}H_3-\overset{\delta+}{Mg}-Br \longrightarrow CH_3-\underset{CH_3}{\overset{H}{C}}-\bar{O}\overset{+}{Mg}Br \xrightarrow[\overset{\delta+}{H}-\overset{\delta-}{OH}]{H^+}$$

$$CH_3-\underset{CH_3}{\overset{H}{C}}-OH+Mg\begin{matrix}OH\\Br\end{matrix}$$

2) With Esters



Reaction type: Nucleophilic Acyl Substitution then Nucleophilic Addition

Elaboration:

i) Carboxylic esters, R'C02R'', react with 2 equivalents of organolithium or Grignard reagents to give tertiary alcohols.

ii) The tertiary alcohol contains 2 identical alkyl groups (see R)

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.

REACTION OF RLI or RMgx WITH AN ESTER

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 CII.; 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 electrophilic 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 CO_2 (Carbonation of Grignard Reagents, RMgX) Nucleophilic Addition of Rmgx to Carbon Dioxide

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.

Q12. What are amines? Give their Nomenclature preparation & properties.

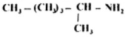
Answer

Nomenclature of Amines:

1) Common System of Naming

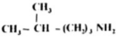
The common names of amines are written by adding the suffix-amine to the name of alkyl or aryl radicals.

$CH_3CH_2NH_2$ — **Ethyl amine**

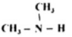


$CH_3-(CH_2)_3-\underset{CH_3}{\underset{|}{CH}}-NH_2$ — **Sec-hexyl amine**

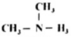
(a primary amine,
sec-indicates secondary group)



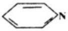
$CH_3-\overset{CH_3}{\overset{|}{CH}}-(CH_2)_3NH_2$ — **Iso-hexyl amine**
a primary amine
(Iso-represents redical)



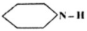
$CH_3-\overset{CH_3}{\overset{|}{N}}-H$ — **Dimethyl amine (a sec-amine)**



$CH_3-\overset{CH_3}{\overset{|}{N}}-H_3$ — **Trumethly amine (a ter-amine)**

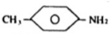


Pyridine (a ter-amine)

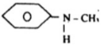


Pyridine

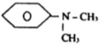
Aniline, $C_6H_5NH_2$ containing methyl group on the ring is called Toluidine. If there is some alkyl group substituted in —NH2 its name is represented by writing N-(alkyl group). It indicates that alkyl group is located on N-atom and not on the ring. It there are two substituents on N, it is repeated twice,



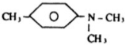
p-toluidine



N-methyl aniline



N, N-dimethyl aniline



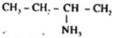
N, N-dimethyl
p-toluidine

2) IUPAC System of Naming

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.

CH_3NH_2

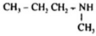
Amino methane



$CH_3-CH_2-\underset{NH_2}{\underset{|}{CH}}-CH_3$

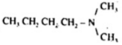
2-Aminopropane

Secondary and tertiary amines are named by using a compound prefix that includes the names of all but the largest alkyl group.



$CH_3-CH_2CH_2-\underset{CH_3}{NH}$

Methyl amino propane



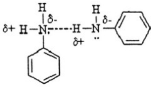
$CH_3CH_2CH_2CH_2-N(CH_3)_2$

(Dimethyl amino butane)

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, see below, or other H-bonding systems (e.g. water). The implications of this are:

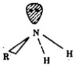
- high melting and boiling points compared to analogous alkanes
- high solubility in aqueous media

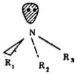


intermolecular H-bonding in amines

Structure:

In amines, nitrogen atom is sp^3-hybridized and has nearly tetrahedral structure. It forms three sigma bonds with its three sp3-hybrid orbitals while the fourth non-bonding sp3hybrid carries a pair electron





(Such tertiary amine is optically active)

The non-bonding electron 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 of amines:

Amines may act as bases towards acids and as Nucleophiles towards electrophile. They are more basic than alcohols and ethers and they are also more nucleophilic, e.g., ether does not react whereas at the same temperature amines gives addition product with $CH_{3\text{-}I}$,

$$C_2H_5OC_2H_5 + CH_{3\text{-}I} \rightarrow \text{No reaction}$$

$$(C_2H_5)_3N + CH_3I \rightarrow [(C_2H_5)_3NCH_3]^+I^-$$

Prepration of Amines

1) Alkylation of Ammonia by Alkyl Halides

$$R-X + 2NH_3 \rightarrow R-NH_2 + Nh_4X^-$$

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,

$$NH3 + R-X \rightarrow (R-NH_3)^+ X \xrightarrow{Base} R-NH_2 + HX$$

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

$$C2H5 - I + NH3 \longrightarrow C2H2 - NH2 + HI$$

$$C2H5 - I + C2H5 - NH3 \longrightarrow C2H5 - \underset{\underset{H}{|}}{N} - C2H5 + HI$$

$$C2H5 - I + C2H5 - \underset{\underset{H}{|}}{N} - C2H5 \longrightarrow (C2H5)3 - N + HI$$

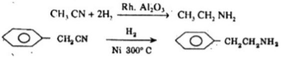
$$(C_2H_5)_3N + C_2H_5I \rightarrow (C_2H_5)_4NI^+$$

At the end of the reaction, addition of strong alkali such as KOH liberates free amines from heir 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.

2) Reductions of nitrogen containing functional groups:

1) Reduction of Nitriles

Reduction of alkyl or aryl nitriles gives primary amines. The reduction may be brought about by LiAlH4, or sodium in ethanol. Catalytic hydrogen with Rh-A1203, Pt or Raney nickel may also be employed to get primary amines

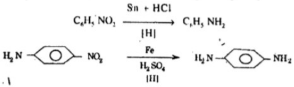


$$CH_3CN + 2H_2 \xrightarrow{Rh.\ Al_2O_3} CH_3CH_2NH_2$$

ii) Reduction of Nitro Compounds

$$\underset{\text{Nitroarene}}{Ar-NO_2} \xrightarrow{[R]} \underset{\text{primary aryl amine}}{Ar-\ddot{N}H_2}$$

Nitro compounds on catalytic or chemical reduction produce primary amines

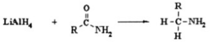


$$C_6H_5NO_2 \xrightarrow[\text{[H]}]{Sn + HCl} C_6H_5NH_2$$

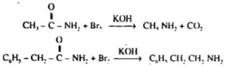
- Nitroarenes can be reduced to primary aryl amines (see scheme).

- Typical reducing agents include, Fe / H+, Sn / H+ or catalytic hydrogenation (e.g. H2 /

Reduction of Amides



An amide on treatment with Bromine in the presence of KOH yields primary amines. The reaction occurs through rearrangement.



$$CH_3-\overset{O}{\overset{\|}{C}}-NH_2+Br_2\xrightarrow{KOH}CH_3NH_2+CO_2$$

$$C_6H_5-CH_2-\overset{O}{\overset{\|}{C}}-NH_2+Br_2\xrightarrow{KOH}C_6H_5CH_2CH_2NH_2$$

Reactivity:

Amines are basic and Nucleophiles because of non-bonding pair of electrons on nitrogen. The relative availability of this pair of electrons 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 pkb, i.e.

pkb = - logkb

For ammonia and methyl amine, the pkb values are

$pkNH_3 = 4.76$; $pkCH_3NH_2. = 3.38$

Since $pkNH_3 < pkCH_3NH_2$ methyl amine is a stronger base than ammonia. It can be explained as under:

In ammonia, the pair of electrons by s-orbitals of hydrogen atoms where as in CH_3NH_2, sp^3 - orbital of carbon pushes electrons towards nitrogen.

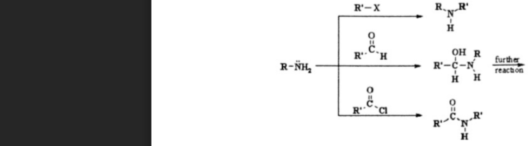
Therefore, the pair of electrons on nitrogen is relatively more available in methyl amine than in ammonia. The methyl ammonium ion, $CH_3NH_3^+$ is stabilized due to electron donating inductive effect of the methyl group. On the other hand, NH_4^+ ion is not stabilized by hydrogen atoms. Both these factors favor methylamine to a stronger base than ammonia.

Higher members show deviation to these arguments. It is because the stabilization of a positive ion also depends upon the extent of salvation, hydrogen bonding and resonance stabilization. Moreover, the availability of non-bonding pair of electrons is also affected by steric factor in addition to these aspects

REACTIONS OF AMINES

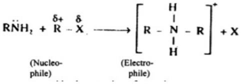
The important organic reactions of amines (nucleophiles) are with the common electrophiles:

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



Alkylation of Amine by Alkyl Halides

"The alkylation of alkyl is called alkylation". It produces sec- or tertiary am9ine,"



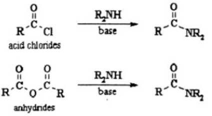
$R_2NH_2^+$ loses a proton with a base to give a free amine.

2) **Reactions of Primary Amines with Aldehydes and Ketones**

Aldehydes and ketones react with primary amines o form Schiff's base, e.g.,

$$CH_3CH_2 - NH_2 + CH_3CHO \rightarrow C_2H_5 - N = CH - CH_3$$

3) **Preparation of Amides**



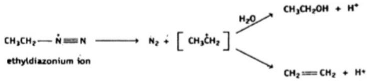
4) **Preparation of Diazonium Salts**

When amines react with nitrous acid, diazonium compounds are formed.

$$RNH_2 + HNO_2 \longrightarrow R - N\equiv N + OH + H_2O$$

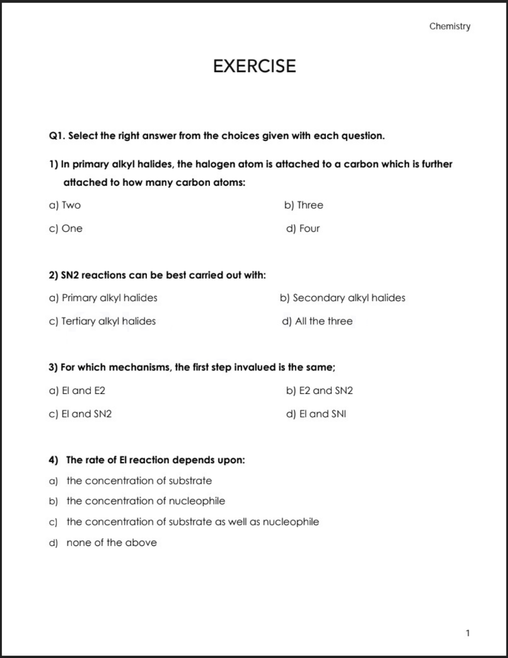
Diazonium ion

The diazonium group, group is rather unstable. In the case of the ethyldiazonim ion, it decomposes at once:



When the group is attached to a benzene ring, though, the ion is stabilized to some extent by the delocalized electron of the ring. The benzene diazonium ion is therefore much more stable than its aliphatic counterparts. Nevertheless, it decomposes readily above I0°C.

Primary amines, **R-NH₂** or **ArNH₂**, undergo nucleophilic addition with aldehydes or ketones to give **carbinolamines** which then dehydrate to give substituted **imines**.



EXERCISE

Q1. Select the right answer from the choices given with each question.

1) 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

2) SN2 reactions can be best carried out with:

a) Primary alkyl halides	b) Secondary alkyl halides
c) Tertiary alkyl halides	d) All the three

3) For which mechanisms, the first step invalued is the same;

a) El and E2	b) E2 and SN2
c) El and SN2	d) El and SNI

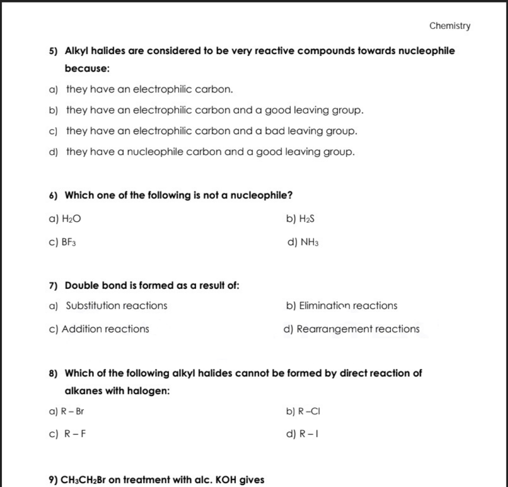
4) The rate of El reaction depends upon:

a) the concentration of substrate

b) the concentration of nucleophile

c) the concentration of substrate as well as nucleophile

d) none of the above



5) Alkyl halides are considered to be very reactive compounds towards nucleophile 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 nucleophile carbon and a good leaving group.

6) Which one of the following is not a nucleophile?

a) H_2O	b) H_2S
c) BF_3	d) NH_3

7) Double bond is formed as a result of:

a) Substitution reactions	b) Elimination reactions
c) Addition reactions	d) Rearrangement reactions

8) Which of the following alkyl halides cannot be formed by direct reaction of alkanes with halogen:

a) R – Br	b) R –Cl
c) R – F	d) R – I

9) CH_3CH_2Br on treatment with alc. KOH gives

a) Propanal b) Propene

c) Propane d) None

10) Grignard's reagent gives alkane with:

a) water b) Ethylamine

c) Ethanol d) All of these

11) Action of alkyl halides with Na metal yield;

a) Alkanes b) Alcohols

c) Alkenes d) Phenols

12) Alkyl halides react with excess of ammonia to give;

a) 1^0 — amine b) 2^0 — amine

c) 3^0 — amine d) all

13) Among the alkyl halides the primary alkyl halides always follow the mechanism.

a) SNI b) SN2

c) SN3 a) SN4

14) Grignard's reagent on treatment with chloramines gives;

a) Acetamide b) Primary amine

c) Secondary amine d) Urea

15) Nucleophilic addition of a primary amine gives;

a) Imine b) Urea

c) Ammonia d) Nitrobenzene

Answers

1)	c)	2)	c)	3)	d)	4)	a)	5)	b)
6)	c)	7)	b)	8)	d)	9)	b)	10)	d)
11)	a)	12)	c)	13)	b)	14)	b)	15)	a)

Q2. Give short answers of the following questions.

Q1. What are primary, secondary and tertiary alkyl halides?

Answer

Please see Answer of Q no 18 of chapter notes.

Q2. Why alkyl iodides cannot be prepared by directly heating iodine with alkene?

Answer

(i) Iodine on reaction with alkenes produced iodoalkanes which are unstable and decompose again to give I2.

(ii) The second factors are strong wanderwal's among 12 molecules due to strong wanderwal's forces among 12 molecules the reactivity of 12 in alkanes decreases.

(iii) Also, the addition of 12 to an alkene produces dihalides and not alkyl halides.

Q3. What are Nucleophilic substitution reactions or SN reactions?

Answer

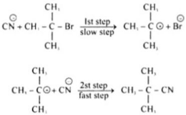
Please see answer of Q6 of chapter notes.

Q4. Tertiary alkyl halides shoe SNI reactions mostly, why?

Answer

Tertiary alkyl halides on reaction with nucleophile are converted into the product. It means in one step there occurs one change so that is why it is called SNI reaction.

For example



$$\overset{\odot}{CN} + CH_3-\underset{CH_3}{\overset{CH_3}{C}}-Br \xrightarrow[\text{slow step}]{\text{Ist step}} CH_3-\underset{CH_3}{\overset{CH_3}{C}}\odot + \overset{\odot}{Br}$$

$$CH_3-\underset{CH_3}{\overset{CH_3}{C}}\odot + \overset{\odot}{CN} \xrightarrow[\text{fast step}]{\text{2st step}} CH_3-\underset{CH_3}{\overset{CH_3}{C}}-CN$$

Q5. What are elimination reactions?

Answer

Please see answer of Q 13 of chapter notes.

Q6. Which factor decides the reactivity of alkyl halides?

Answer

Please see answer ofQ2 of chapter notes.

Q7. What are the diazonium salt?

Answer

Please see answer of Q47 of chapter notes.

Q8. How can nucleophilic addition of a primary amine be giving an amine?

Answer

Primary amines on reaction with aldehydes and Ketones on condensation give an imine which is called Schiff base

$$C_2H_5NH_2 + CH_3CHO \xrightarrow{H^+} C_2H_5N = CH - CH_3$$

$$C_6H_5NH_2 + CH_3CHO \xrightarrow{H^+} C_6H_5N = CH - CH_3$$

Q9. Amines are more basic than analogous alcohols, why?

Answer

Please see answer of Q39 of chapter notes.

Q10. How tertiary alcohols are obtained from R—Mg—X?

Answer

Please see answer of Q30 of chapter notes.

Q3. Give detailed answers for the following questions.

Q1. Discuss the reactivity of alkyl halides.

Answer

Please see answer ofQ2 of Chapter notes.

Q2. Give three methods for the preparation of alkyl halides?

Answer

Please see answer of QI of Chapter notes.

Q3. Explain in detail SNI and SN2 reactions with mechanism.

Answer

For SNI reaction Please see answer of QIO of chapter notes for SN2 reaction please see answer of QI 0 of chapter notes.

Q4. What are P— elimination reactions? Explain them with detail.

Answer

Please see answer of Q 13 of Chapter notes.

Q5. How will you convert ethyl chloride to the

i) Ethyl cyanide ii) Ethanol iii) Propane iv) N-butane

v) Tetraethyl lead

Answer

(I) Ethyl chloride into Ethyl cyanide:

$$CH_3 - CH_2 - Cl + Nach \rightarrow CH_3 - CH_2 - CH + Nacl$$

(II) Ethyl chloride into Ethanol:

$$CH_3 - CH_2 - Cl + Koh \rightarrow CH_3 - CH_2 - CH + Kcl$$

(III) Ethyl chloride into Propane:

$$CH_3 - CH_2 - \boxed{Cl + 2Na + Cl} - CH_3 \rightarrow CH_3 - CH_2 - CH_2 + Nacl$$

(IV) Ethyl chloride into N-butane

$$CH_3 - CH_2 - Cl + 2Na + Cl - CH_2 - CH_3 \rightarrow CH_3 - CH_2 - CH_2 - CH_3 + 2Nacl$$

(v) Ethyl chloride into tetraethyl lead:

$$Na_4 / Pb + 4C_2H_5 - Cl \rightarrow (C_2H_5) Pb + 4Nacl$$

Q6. Discuss the preparation and reactivity of Grignard's reagent?

Answer

Please see answer of Q29 of chapter notes.

Q7. What are the amines? Gives nomenclature.

Answer

Please see answer of Q36 of chapter notes.

Q8. What are the main features which increase the basicity of amine?

Answer

Please see answer of Q44 of chapter notes.

Q9. Amides are reduced by LiAlH4. Give mechanism.

Answer

Please see answer of Q43 of chapter notes.

Q10. What are the diazonium salts? How they can be prepared? Give their reactions.

Answer

Please see answer of Q47 of chapter notes.

Multiple Choice Questions

1) Alkyl halide are compounds in which one hydrogen atom of alkanes has been replaced by replaced by:

a) One halogen atom
b) two halogen atom
c) three halogen atom
d) four halogen atoms

2) Those haloalkanes which contains one halogen atom called:

a) Dihaloalkane
b) Monohaloalkane
c) Trihaloalkane
d) Tetrahaloalkane

3) Alkyl halides in which halogen atom is attached with primary carbon are called:

a) Primary halides
b) Secondary halides
c) Tertiary halides
d) Quaternary halides

4) Alkyl halides in which halogen atom is attached with a secondary carbon atom are called:

a) Primary halide
b) Secondary halides
c) Tertiary halides
d) Quaternary halides

5) Alkyl halides in which halogen atom is to atertiary carbon is called:

a) Primary halide
b) Secondary halides
c) Tertiary halides
d) Quaternary halides

6) The functional group of alkyl halide is:

a) sp^3 hybridized
b) sp^2 hybridized
c) sp hybridized
d) both a & b

7) Which factors which control the reactivity of alkyl halide:

a) Bond polarity of C-X bond
b) Bond polarity of C-H bond
c) Bond energy of C-X bond
d) Both of a and c

8) The electronegativity of fluorine is:

a) 4.0
b) 3.5
c) 3.1
d) 2.8

9) Which is an electron rich species that will react with an electron poor species:

a) electrophile
b) Nucleophile
c) Leaving group
d) both a & b

10) The two fundamental events in a nucleophilic substitution reaction are:

a) Formation of new bond to the nucleophile

b) Breaking of the leaving group

c) Both a & b

d) None of these

11) The molecule or substance to which nucleophile attacks is called:

a) Substrate molecule

b) Leaving group

c) Electrophile

d) Both a & b

12) The substance which departs with an unshared pair of electrons is called:

a) electrophile

b) leaving group

c) nucleophile

d) Both a & b

13) The leaving group in which the incoming nucleophile is stronger than the departing one is called:

a) poor leaving groups

b)leaving group

c) good leaving group

d)None of these

14) Which is the nucleophile:

a) C_2H_5O

b) H_2O

c) Both of these

d) H_3O

15) Which of below are good leaving group:

a) NH_3

b) Br^-

c) F

d) RO_-

16) Which of below are poor leaving group:

a) NH_3

b) Cl_-

c) H_2O

d) T_5O_-

17) The substitution nucleophilic unimolecular two step reaction is:

a) SN_2

b) SN_I

c) SN_3

d) Both of these

18) The rate of SNI reaction depends upon the concentration of:

a) Electrophiles

b) Alkyl halides

c) Alkanes

d) Alcohols

19) The substitution nucleophilic bimolecular reaction which occurs in one step is called:

a) SN_2

b) SN_I

c) Both a & c
d) SN_3

20) The rate of SN2 reaction depends upon the concentration of:

a) Electrophiles
b) Nucleophile
c) Alkyl halides
d) None of these

21) In SNI mechanism inversion of configuration takes place:

a) 50%
b) 60 %
c) 70 %
d) 100%

22) In SN_2 mechanism inversion of configuration take place at:

a) 70 %
b) 50 %
c) 100 %
d) 60 %

23) The chemical reaction in which two groups are eliminated from two adjacent atom is called:

a) Elimination reaction
b) Subsitution reactions
c) Halogenation reaction
d) Name of these

24) The unimolecular two step elimination reaction is called:

a) E2 mechanism
b) El mechanism
c) SNI mechanism
d) SN2 mechanism

25) The bimolecular one step elimination reaction is callec

a) E2 mechanism
b) SN2 mechanism
c) SNI mechanism
d) All of the above

26) The rate of El mechanism depends upon the concentration of:

a) Substrate
b) Nucleophile
c) Electrophile
d) Leaving group

27) The rate of E2 mechanism depends upon the concentration of:

a) Substrate
b) Base
c) Electrophile
d) Both a & b

28) Those alcohols in which there is one halogen atom is called:

a) Monohydric alcohols
b) Dehydric alcohols
c) Trihydric alcohols
d) None of these

29) Aniline, C6H5Nh2 containing methyl group on the ring is called:

a) Pyridine
b) Toluidine
c) Aspirin
d) Mestylene

30) Alkyl or aryl radicals are called:

a) Amines
b) Arines
C) Amides
d) Both a & b

31) In amines the nitrogen atom is:

a) sp^2 hybridized
b) sp3—hybridized
C) sp hybridized
d) sp4—hybridized

32) Which is used as an antifungal and antiseptic agent:

a) Thiomersal
b) Salvation
c) Arene
d) Cisplatin

33) Which are kinetically inert and used for the design of new radiopharmaceuticals:

a) Tamoxifen
b) Arene
c) Salvarsan
d) Cisplatin

34) Which is an anticancer compound:

a) Tamoxifen
b) Thiomersal
c) Arene
d) Salvarsan

35) Which is an anti-syphilis medication:

a) Merbromin
b)Salvarsan
c) Arene
d)Thiomersal

36) Which compound is formed when amines react with vitrous acid?

a) Benzene
b) Mesityle
c) Diazonium
d) Thiolene

37) The benzene diazonium ones readily decomposes above:

a) 20°C
b) 10°C
c) 40°c
d) 5°C

38) Which is used as anesthetic:

a) Ethyl chloride
b) Methyl chloride

c) Propanol d) Butyl chloride

39) Erupting volcanoes exit large quantities of:

a) Hydrocarbons b) Halogens

c) Halides d) Both a and c

40) CD's are made from:

a) Proponyl chloride b) Ethyl chloride

c) Vinyl chloride d) Acetyl chloride

Answer

l)	a)	2)	b)	3)	a)	4)	b)
5)	c)	6)	a)	7)	d)	8)	a)
9)	b)	10)	?)	11)	a)	12)	b)
13)	c)	14)	c)	15)	b)	16)	a)
17)	b)	18)	b)	19)	a)	20)	b)
21)	a)	22)	c)	23)	a)	24)	b)
25)	a)	26)	a)	27)	d)	28)	a)
29)	b)	30)	a)	31)	b)	32)	a)
33)	b)	34)	a)	35)	b)	36)	c)
37)	b)	38)	a)	39)	d)	40)	c)

Give Short Answer

QI: What are alkyl halides?

Answer

Alkyl halides are the compounds in which one hydrogen atom of alkanes has been replaced by one halogen atom.

Q2: What are primary alkyl halides? Give examples.

Answer

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

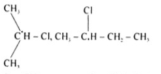
Example: $CH_3 - Cl$, $CH_3 - CH_2 - Cl$

Q3: What are secondary alkyl halides? Give examples.

Answer

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

Example:



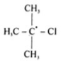
2 — Chloropropane   2 — Chlorobutane

Q4: What is tertiary alkyl halide? Give example.

Answer

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

Example:



$$H_3C - \overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{\overset{|}{\underset{|}{C^*}}}} - Cl$$

t — Butyl chloride

Q5: Why alkyl halides have higher melting & Boiling points compared to alkanes?

Answer

Because of the presence of polar bond which creates a molecular dipole that raises the melting and boiling points compared to alkanes.

Q6: Give reaction which illustrate the conversion of alcohols into the alkyl halides.

Answer

$$CH_3-CH_2-OH + HX \xrightarrow{Z.ncl} CH_3-CH_2-X + H_2O$$

Ethylhalide

Q7: What are the factors which control the reactivity of alkyl halides.

Answer

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

i — Bond polarity of C — X bond

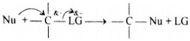
ii — Bond energy of C — X bond

Q8: Briefly explain "Nucleophilic substitution reaction".

Answer

Nucleophilic substitution reaction occurs when an electron rich species, the nucleophile reacts at an electrophilic C-atom attached to an electronegative group.

i.e



Q9: What are two fundamental events in a nucleophilic substitution reactions?

Answer

These are as follows

i. Formation of new s bond to the nucleophile.

ii. Breaking of the living group.

Q 10: What are nucleophiles? Give examples.

Answer

The species which are rich in electron have unshared pair of electrons available for bonding and negatively or nature charged is called nucleophile. Example: HO- C2H50- , Hs-, H20

Q11: Define substrate?

Answer

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

Q12: What is leaving group?

Answer

The group which departs with an unshared pair of electrons is called leaving group.

Q13: What are good leaving groups and poor leaving groups? Give examples.

Answer

The incoming nucleophile must be stronger than the departing one good leaving groups.

Examples: Cl-, Br-, r.etc

The groups in which the incoming nucleophile are not stronger than the departing one are poor leaving groups

Examples: Off, OR, NH2- etc

Q14: What is SNI Mechanism?

Answer

It is substitution nucleophilic bimolecular two step reaction.

$$R - X \underset{}{\overset{\text{slow}}{\rightleftharpoons}} R^{+} + X^{-}$$

$$R^{\cdot} - Nu \xrightarrow{\text{Fast}} R - Nu$$

Q15: What is SN_2 Mechanism?

Answer

It substitution nucleophilic bimolecular reaction which occurs in one step.

$$Nu + CH_{1} - X \longrightarrow Nu - CH_{1} + X$$

Q16: What are elimination reactions?

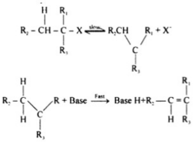
Answer

The cnemical reaction in which two groups are eliminated from two adjacent atom is called elimination reaction. Since ß-hydrogen is necessary (or eliminations, it is called P-elimination.

Q17: What is Er mechanism?

Answer

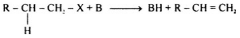
It is unimolecular two step elimination reactions



Q18: What is Ez mechanism?

Answer

It is bimolecular one step elimination reaction



$$R-\underset{\substack{|\\H}}{CH}-CH_2-X+B \longrightarrow BH+R-CH=CH_2$$

Q19: Under which condition the elimination reaction occurs?

Answer

Elimination reaction occurs only when the substance has ß-hydrogen.

Q20: What is sp³ hybridized?

Answer

The process in which three-p orbitals and one-s orbital combine together to give sp3 hybrid orbital this is called sp³ hybridization.

Q21: Define Bond energy?

Answer

The energy which is required to form a bond is called bond energy.

Q22: What are monohaloalkanes? Give example.

Answer

Those alkanes which have single or when halogen group attached to it are called monohaloalkanes.

Example:

H

|

H – C – X

|

H

Q23: How Grignard's reagents are prepared?

Answer

Magnesium metal cut into small pieces is added to a solution on of an alkyl halide or aryl halide in only dry either. 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.

$$R-X+Mg \xrightarrow[\text{Either}]{\Delta} RMgX$$

Q24: Why Grignard reagents are nucleophile?

Answer

Grignard reagents are nucleophile because of the presence of partial negative charge on the carbon of alkyl group.

Q25: What are Amines? Give example.

Answer

Alkyl or aryl radicals having amine group are called Amines

Example: $CH_2 - CH_2 - NH_2$

Ethylamine

Q26: Why Amines are polar?

Answer

Amines are the polar substance because of the polar nature of bond which results in formation of hydrogen bonds with other H-bonding systems.

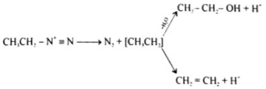
Q27: What is Diazonium salt?

Answer

When amines react with nitrous acid, diazonium, compound is formed.

$$RNH_2 + HNO_2 \rightarrow R - N \equiv N - OH + H_2O$$

The diazonium group is rather unstable, it decomposes



Q28: What 'is the use of arena and cyclopentadienyl?

Answer

They are kinetically inert and used for the design of new radiopharmaceuticals.

Q29: What is use of Thermersal?

Answer

It is an antifungal and antiseptic agent and used as a vaccine preservative in immunoglobulin preparations and rasal products.

Q30: What is haemoglobin

Answer

Haemoglobin is the oxygen carrier pigment found in the blood of animals and humans.

Q31: What is chlorophyll?

Answer

Chlorophyll is the green pigment in plants which is receptor of light energy during photosynthesis.