CHAPTER 17

ALKYL HALIDES AND AMINES

After completing this lesson, you will be able to:

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

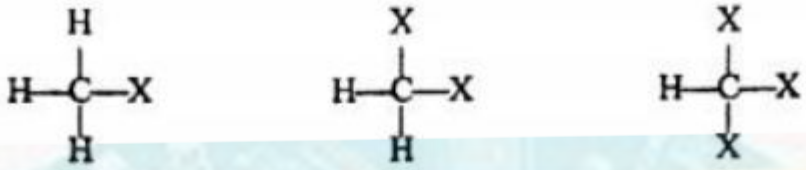
Q1. What are alkyl Halides? Explain with examples.

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"Alkyl halides are the compounds in which one hydrogen atom of Alkanes has been replaced by one halogen atom.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



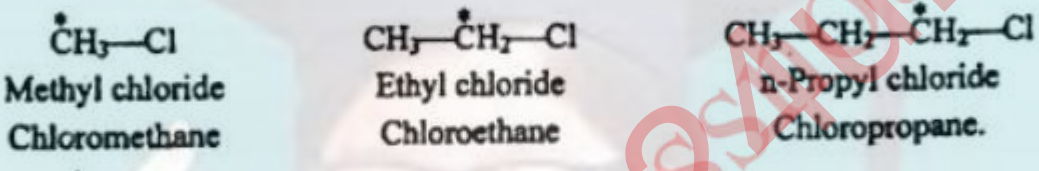
Monohaloalkane Dihaloalkane Trihaloalkane

Classification of Alkyl Halides:

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

i) Primary Alkyl Halides:

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



Methyl chloride
Chloromethane

Ethyl chloride
Chloroethane

n-Propyl chloride
Chloropropane.

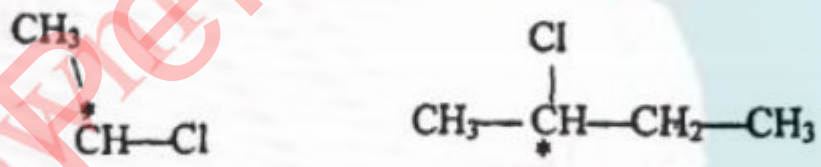
(Ċ is primary carbon atom)

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."



Iso-Propyl chloride
2-Chloro propane

Sec-Butyl chloride
2-Chlorobutane.

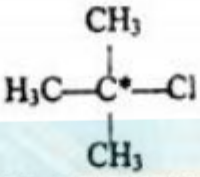
(Ċ is secondary carbon atom)

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".



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

(C• is tertiary C-atom)

Nomenclature of Alkyl halides

Alkyl halides are named according to the following systems:

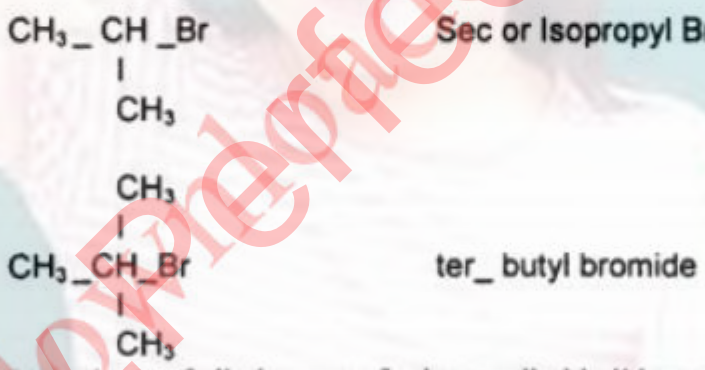
i) Common System of naming.
ii) IUPAC System of naming.

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,.



Sec or Isopropyl Bromide

ter_ butyl bromide

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,

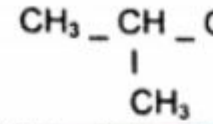
$CH_3\_CH_2\_CH_2\_CH_2\_Br$ n_butyl bromide

II) IUPAC System of naming.

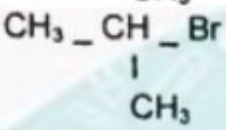
According to this system alkyl halides are named as derivatives of alkanes. The following rules are observed for this purpose:

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, e.g,.

$CH_3\_CH_2\_CH_2\_CH_2\_Br$ Bromo butane

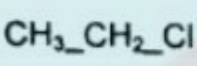


2-bromo_3_methyl butane

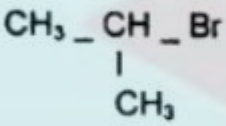


2-bromo propane

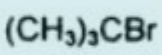
The names given below are also accepted by the IUPAC



Ethyl Chloride



Iso_propyl Bromide



ter_butyl bromide

Q2. Give Physical Properties of Alkyl Halides

Answer

1) 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 bonds are 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 $ZnCl_2$, which acts as a catalyst.

$$CH_3CH_2-OH + HX \xrightarrow{ZnCl_2} CH_3CH_2-X + H_2O$$

Ethyl halide

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

a) Alcohols react with thioyl chloride 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.

$$ROH + SOCL2 \rightarrow R\text{–}Cl + SO_2 + HCl$$

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

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

$$CH_3–CH_2–OH + PCl_5 \rightarrow CH_3–CH_2-Cl + POCl_3 + HCl$$

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.

$$CH_3.CH_3 + Cl_2 \rightarrow CH_3.CH_2Cl + HCl$$

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:

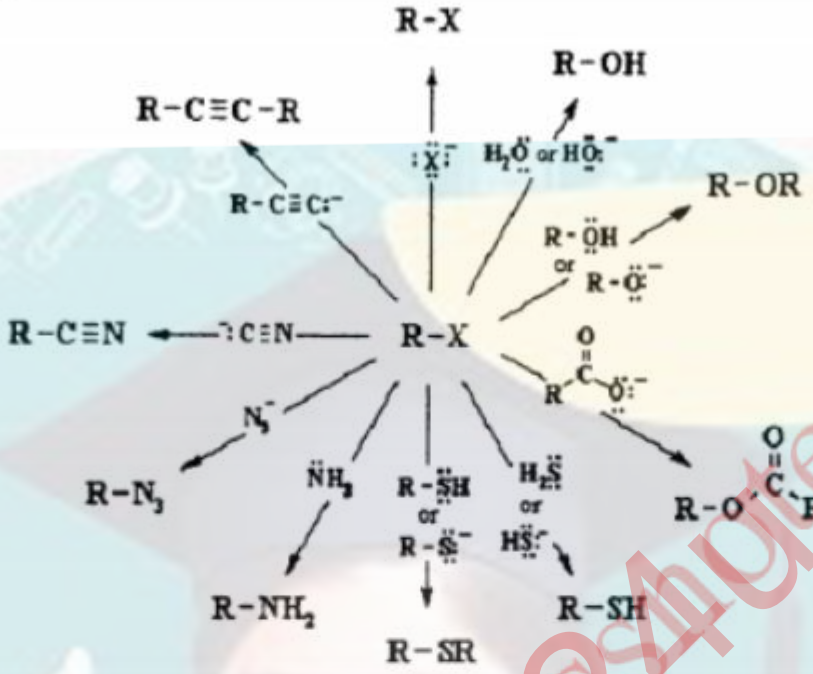
R-iodide > R-bromide > R-chloride > R-fluoride

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.



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 electron 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:

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

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 susbtitution can be represented as follows:

$$Nu^- + \overset{|}{\underset{|}{C}}(\delta+)-LG(\delta-) \rightarrow \overset{|}{\underset{|}{C}}-Nu + LG^-$$

There are two fundamental events in a nucleophilic substitution reaction:

1) 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 preceeds the formation of the new bond : S_N1 reaction
- Simultaneous bond formation and bond breaking : S_N2 reaction

CARBOCATIONS AND THEIR STABILITY

Stability:

The general stability order of simple alkyl carbocations is: (most stable) $3^\circ > 2^\circ > 1^\circ >$ 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 (HX, H_3O^+)

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:

HO^-	Hydroxide ion	NH_2^-	Amino group
$C_2H_5O^-$	Ethoxide ion	Cl^-	Chloride ion
HS^-	Hydrogen sulphide ion	Br^-	Bromide ion
SCN^-	Thio cyanate ion	$\ddot{N}H_3$	Ammonia
$H_2\ddot{O}:$	Water		

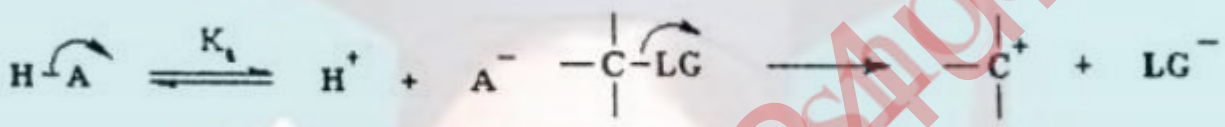
Q6. Define substrate and leaving group.

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^- HSO_4^- are good leaving groups. Poor leaving groups are OH^-, OR and NH^{2-}, 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 S_N1 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 stablization of a LG-.

Here is a table classifying some common leaving groups that we will eventually meet

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

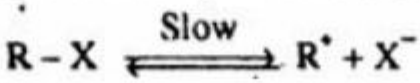
But water itself, H_2O, is a good leaving group, since it is the conjugate base of H_3O^+, which

Q7. Give SN_1 Reaction mechanism.

Answer

SN_1 Mechanism
"It is substitution nucleophilic unimolecular two step reaction."

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



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

$$R^{+} + N\bar{u} \xrightarrow{\text{Fast}} R - Nu$$

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 SN_1 reaction. The brief mechanistic picture of SN_1 reaction base upon the following evidences:

1) Kinetic Evidence:

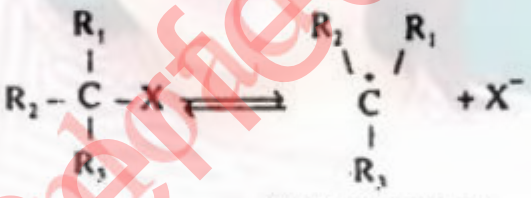
The rate of an SN1 reaction depends upon the concentration of alky halide only. The change is concentration of attacking nucleophile has no effect on the rate

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

It is because the nucleophile combines with the carbonium ion in the second sep. for the same reason, the rate of an SN_1 reaction does not depend on the nature of attacking nucleophile.

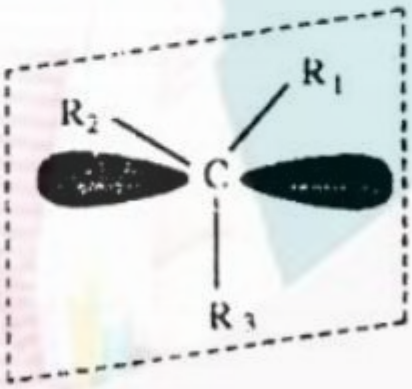
2) Stereo Chemical Evidence:

Experiments have shown that SN1 reaction occur with partial racemization. The extent of partial racemization depends upon several factors including stability f carbonium ion.

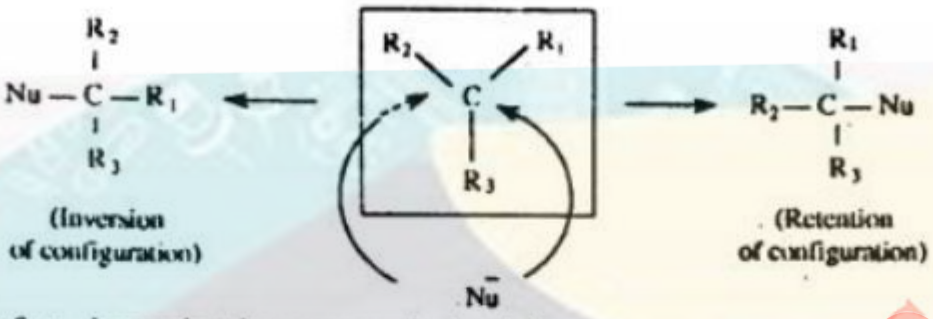


(Carbonium ion)

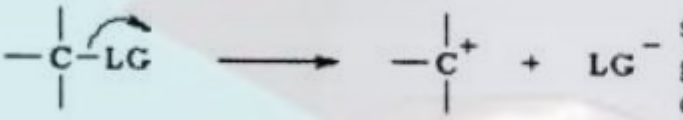
The carbon atom of carbonium ion is sp2 hybridized and carries one empty p-orbital.The nucleophile can attach itself to the p-orbital either on the right or on the left side of carbon with equal ease. The expected product is a recemic mixture. However, the partial recemization suggests a different way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



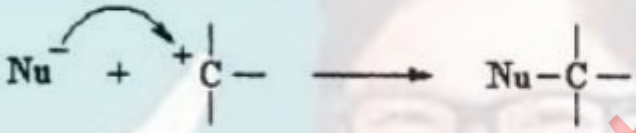
(Planar Carbonium ion)



Therefore, the product has some optical activity.



step 1: slow loss of the leaving group, LG, to generate a carbocation intermediate, then



step 2 : rapid attack of a nucleophile on the electrophilic carbocation to form a new s bond

Q8. Give SN_2 Reaction Mechanism.

Answer

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

Explanation:

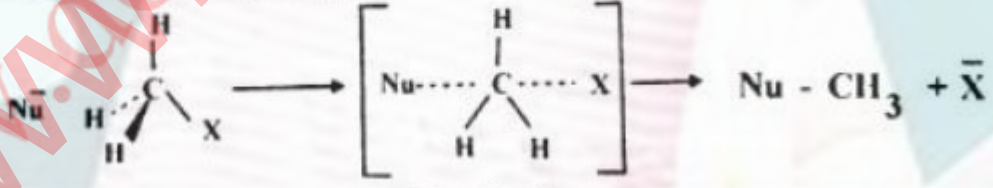
Consider the reaction:

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

(Nucleophile)

Mechanism:

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



Transition state

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

$$Nu^{-} + R-X \longrightarrow Nu-R + X^{-}$$

can be written as

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

Where k = specific rate constant.

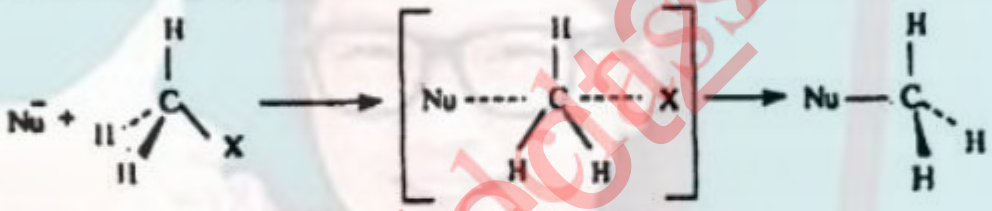
This means that the rate of reaction will be double if the concentration of any of the two is double e.g., the rate of hydrogen.

$$CH_3-Br + OH^{-} \longrightarrow CH_3-OH + Br^{-}$$

Increases when either OH^{-} or CH_3-Br is increased.

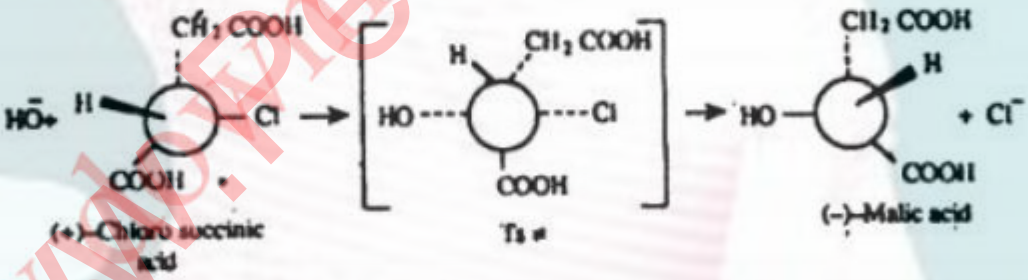
2) Stereo Chemical Evidence:

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 ad the leaving groups are present in the transition state on opposite sides of electrophilic carbon atom.



Transition state

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.



(+)-Chloro succinic acid

Ts ≠

(-)-Malic acid

Comparison of SN1 and SN2 Mechanism

Sr. No.	SN1	Sr. No.	SN2
(1)	It is a two step mechanism.	(1)	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. It is favoured in polar	(3)	It is a bimolecular reaction.

(4)	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?

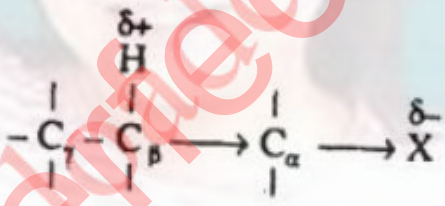
Answer

Definition of Elimination Reaction:

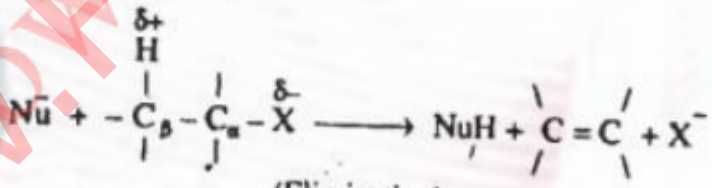
"The chemical reaction in which two groups are eliminated from two adjacent atoms is called elimination reaction". Since β-hydrogen is necessary for eliminations, it is also called β-elimination.

Explanation:

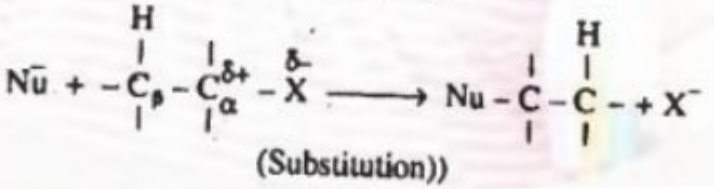
β-hydrogen atom in alkyl halides is slightly acidic due to electron with drawing effect of halogen.



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

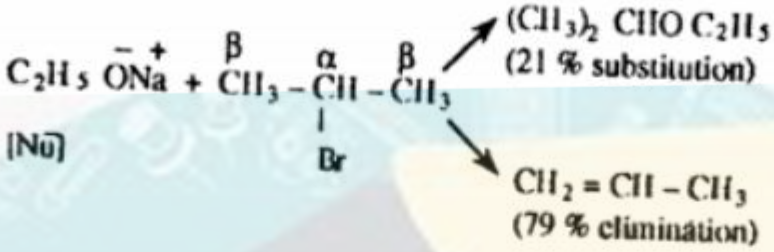


(Elimination)



(Substitution))

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.

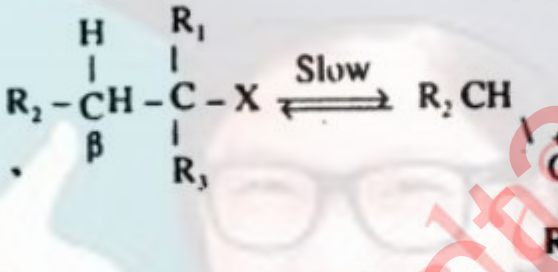


E1 Mechanism

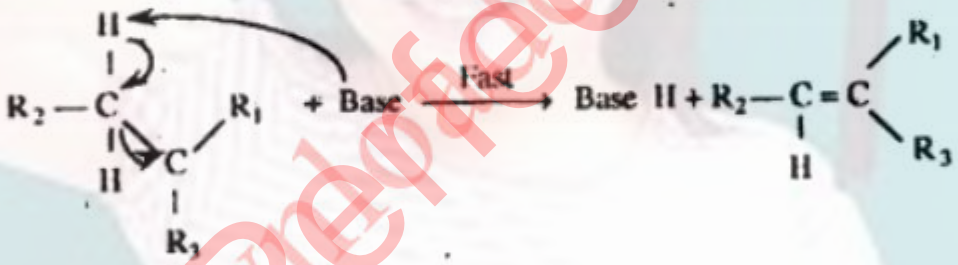
"It is unimolecular two step elimination reactions."

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 β-hydrogen

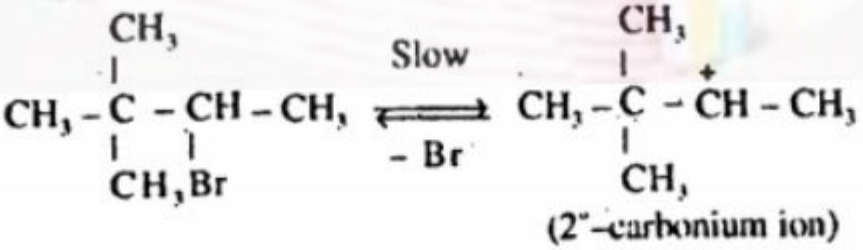


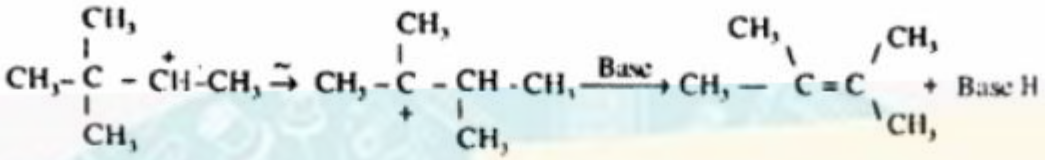
Since only one molecule is undergoing a change in the rate determining step, i.e., first step, this is two step unimolecular elimination reactions.

The 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.

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

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.



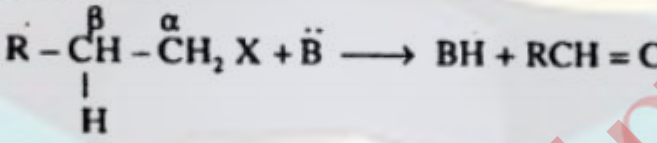


E2 mechanism

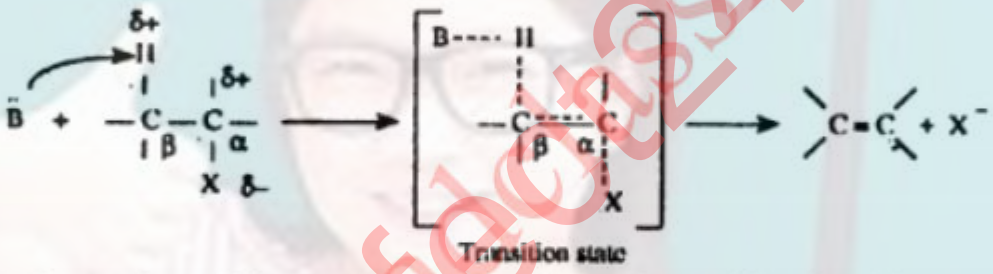
"It is bimolecular one step elimination reaction".

Explanation:

Consider the reaction,



The attacking base removes a proton from the β-carbon simultaneously with the formation of double bond between C_α and C_β and the loss of halide ions.



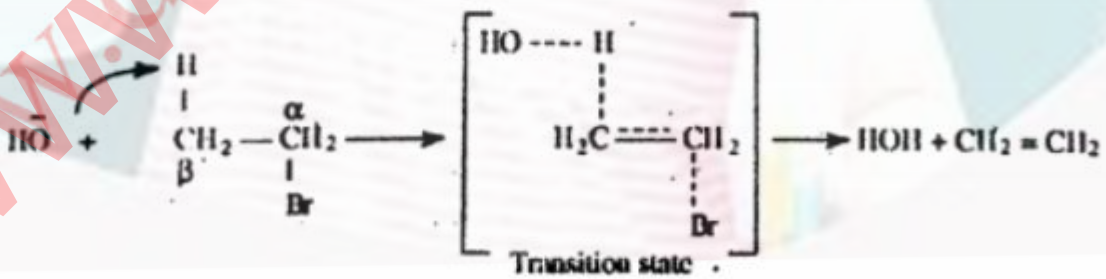
Transition state

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

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

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



Transition state

The rate of reaction follows second order kinetics

$$\text{Rate} = k[CH_3CH_2Br][\bar{O}H]$$

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 α-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.,

$$CH_3 - CH_2\,S(CH_3)_2 + C_2H_5\bar{O}\overset{+}{Na} \xrightarrow[C_2H_5OH]{} CH_3CH_2OC_2H_5 + CH_2 = CH_2$$

(Elimination = 12 %)

$$\begin{matrix}CH_3\\ \\ CH_3\end{matrix}\!\!>\!\overset{+}{S}(CH_3)_2 + C_2H_5ONa \xrightarrow{C_2H_5OH} \underset{\displaystyle CH_3}{CH_2 - CO\,C_2H_5} + CH_3CH = CH_2$$

Subst. 39 % (Elimiantion = 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.

$$-\underset{\displaystyle X}{\overset{\displaystyle H}{\overset{|}{\underset{|}{C}}}} - \underset{|}{\overset{|}{C}} - + \bar{O}H \xrightarrow{E_2} \backslash C = C / + X^- + H_2O$$

(Strong base) (Main product)

$$-\underset{\displaystyle X}{\overset{|}{\underset{|}{C}}} - \underset{|}{\overset{|}{C}} - + CH_3COO^- \longrightarrow -\underset{|}{\overset{|}{C}} - \underset{|}{\overset{|}{C}} - OCOCH_3 + X^-$$

(work –base)

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.,

$$n\text{-}C_{18}H_{37}-X + (CH_3)_3COK \xrightarrow{(CH_3)_3COH} n\,C_{18}H_{37}CH=CH_2 + n\text{-}C_{18}H_{37}OC(CH_3)_3$$

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. E1 is favored by polar solvents like Sn1 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 involve less reorganization of bonds as compared to eliminations, e.g.,

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

at 25°C	17 %	83 %
at 65°C	36 %	64 %

$$CH_3-\underset{\underset{Br}{|}}{CH}-CH_3 + NaOH \xrightarrow[(Bimolecular)]{H_2O} CH_3CH=CH_2 + (CH_3)_2CHOH$$

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 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.

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

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 Grignand'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

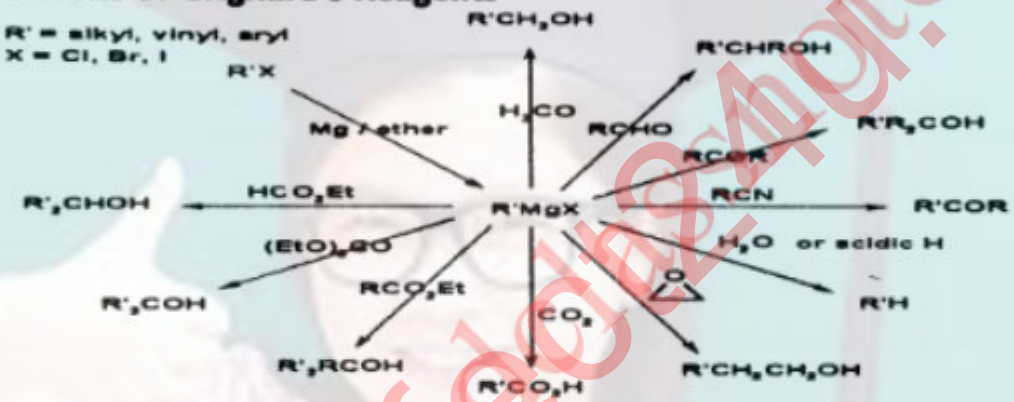
group as a whole bears partial negative charge and organo metallic compounds act as source of nucleophile, e.g.,

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

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

$$\overset{\delta-}{CH_3}-\overset{\delta+}{Mg}-Br + \overset{\delta+}{H}-\overset{\delta-}{OH} \longrightarrow CH_4 + Mg\begin{matrix}/\,OH\\ \backslash\,Br\end{matrix}$$

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 H_3O^+. First two reaction are with aldehydes while third belongs to ketones.

Classification of Monhydric Alcohols:

Monohydric alcohols are classified into the following three families:

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

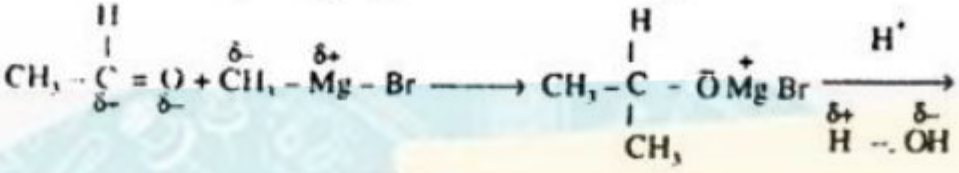
i) Reaction with Methanal (Aldehyde) to form primary alcohol

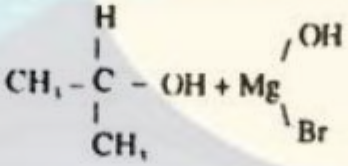
$$H-\overset{\delta+}{\underset{H}{\underset{|}{C}}}=\overset{\delta-}{O} + \overset{\delta-}{CH_3}-\overset{\delta+}{Mg}-Br \longrightarrow CH_3-\underset{H}{\underset{|}{C}}-\ddot{O}\,Mg\,Br$$

(Formaldehyde)

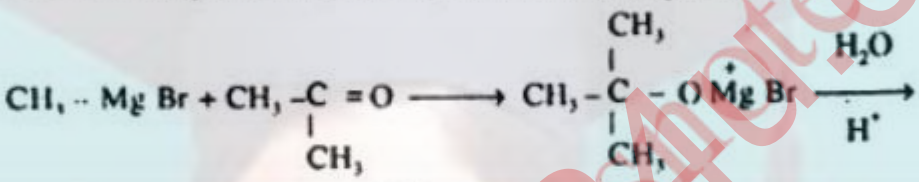
$$\overset{\delta+}{H}-\overset{\delta-}{OH} \longrightarrow CH_3-\underset{H}{\underset{|}{C}}-OH + Mg\begin{matrix}/\,OH\\ \backslash\,Br\end{matrix}$$

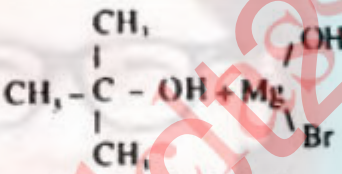
ii) Reaction with Ethanal (Aldehyde) to form secondary alcohol





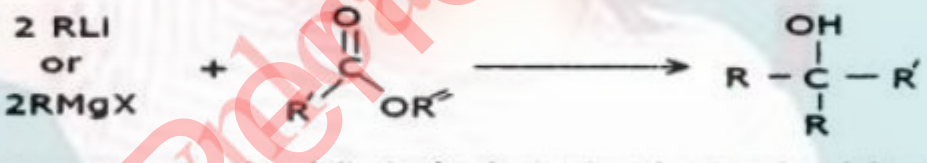
iii) Reaction with Propanone (Ketone) to form tertiary alcohol





(tert–butyl alcohol)

2) With Esters



Reaction type: Nucleophilic Acyl Substitution then Nucleophilic Addition

Elaboration:

i) Carboxylic esters, R'CO_2R", react with 2 equivalent 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.

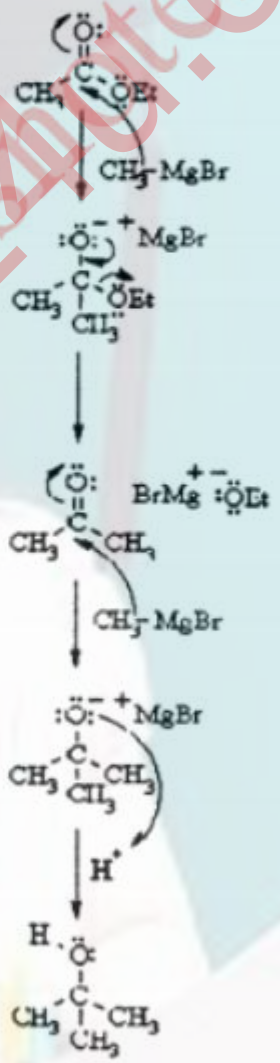
REACTION OF RLi or RMgX WITH AN ESTER

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 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.



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3)With CO_2 (Carbonation of Grignard Reagents, RMgX)

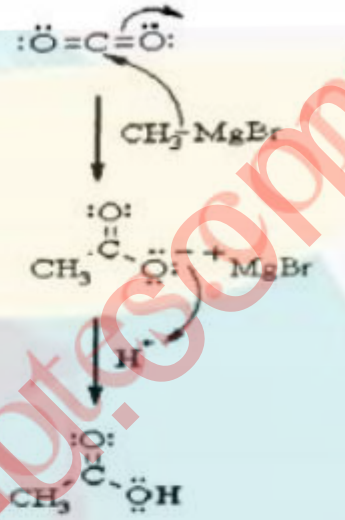
Nucleophilic Addition of Rmgx to Carbon Dioxide

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

$CH_3-(CH_2)_3-CH(CH_3)-NH_2$ — Sec-hexyl amine

(a primary amine.
sec-indicates secondary group)

$(CH_3)_2CH-(CH_2)_3NH_2$ — Iso-hexyl amine
a primary amine
(Iso-represents redical)

$(CH_3)_2NH$ — Dimethyl amine (a sec-amine)

$(CH_3)_3N$ — Trumethly amine (a ter-amine)

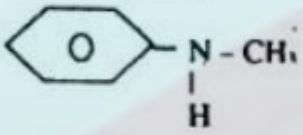
 — Pyridine (a ter-amine)

 — Pyridine

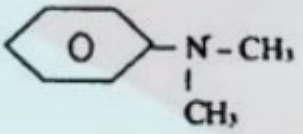
---

Aniline, $C_6H_5NH_2$ containing methyl group on the ring is called Toluidine. If there is some alkyl group substituted in $-NH_2$ its name is represented by writing N-(alkyl group). It indicates that alkyl group is located on N-atom and not on the ring. It there are two substituent on N, it is repeated twice,

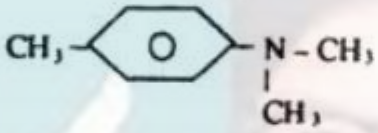
p-toluidine



N-methyl aniline



N, N-dimethyl aniline

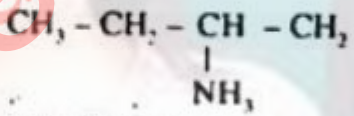


N, N-dimethyl p-toluidine

2) IUPAC System of Naming

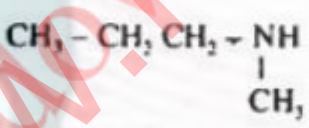
In this system amino group is indicated by a prefix-amino followed by name of hydrocarbons, the position of amino group is indicated by a number obtained by numbering the chain of hydrocarbon.

Amino methane

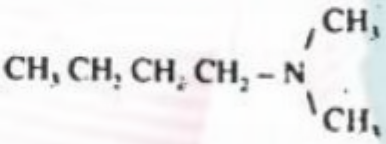


2-Aminopropane

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



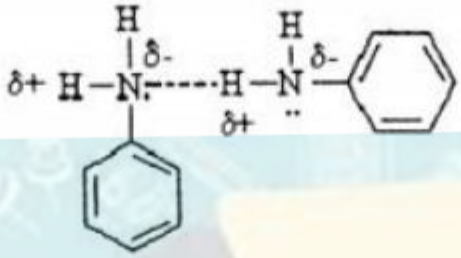
Methyl amino propane



(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 sp3-hybrid 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 where as at the same temperature amines gives addition product with CH_{3-I},

$$C_2H_5OC_2H_5 + CH_{3-I} \rightarrow \text{No reaction}$$
$$(C_2H_5)_3N + CH_3I \rightarrow [(C_2H_5)_3NCH_3]^+I^-$$

Preparation of Amines

1) Alkylation of Ammonia by Alkyl Halides

$$R\text{-}X \quad + \quad 2\,NH_3 \longrightarrow \quad R\text{-}NH_2 \quad + \quad \overset{+}{N}H_4X^-$$

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,

$$\ddot{N}H_3 + R - X \longrightarrow (R - NH_3)^+ \bar{X} \xrightleftharpoons{\text{Base}} R - NH_2 + HX$$

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

$$C_2H_5 - I + NH_3 \longrightarrow C_2H_5 - NH_2 + HI$$

$$C_2H_5 - I + C_2H_5 - NH_2 \longrightarrow C_2H_5 - \underset{\underset{H}{|}}{N} - C_2H_5 + HI$$

$$C_2H_5 - I + C_2H_5 - \underset{\underset{H}{|}}{N} - C_2H_5 \longrightarrow (C_2H_5)_3 - N + HI$$

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

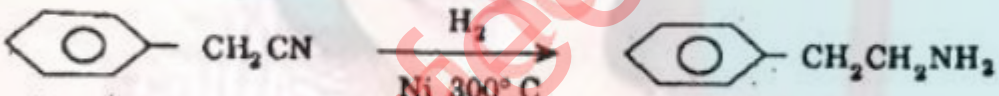
At the end of the reaction, addition of strong alkali such as KOH liberates free amines from heir salts but the quaternary salt is unaffected. The three amines are separated by fractional distillation. Over alkylation can be avoided by using excess of ammonia but the yield is low.

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 $LiAlH_4$, or sodium in ethanol. Catalytic hydrogen with $Rh\text{-}Al_2O_3$, Pt or Raney nickel may also be employed to get primary amines

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

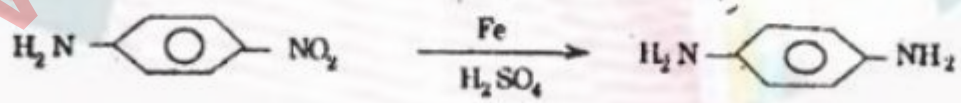


ii) Reduction of Nitro Compounds

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

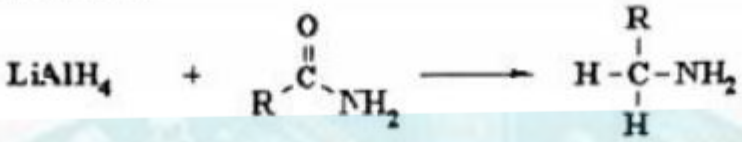
Nitro compounds on catalytic or chemical reduction produce primary amines

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

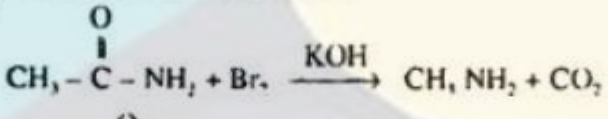


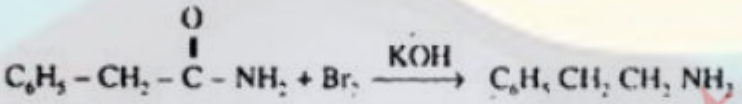
- Nitroarenes can be reduced to primary aryl amines (see scheme).
- Typical reducing agents include, Fe / H^+, Sn / H^+ or catalytic hydrogenation (*e.g.* H_2 / Pd)

Reduction of Amides



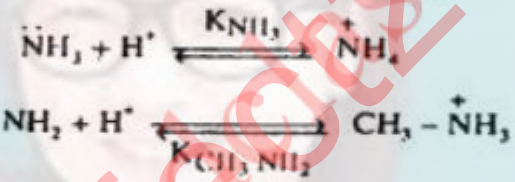
An amide on treatment with Bromine in the presence of KOH yields primary amines. The reaction occurs through rearrangement.





Reactivity:

Amines are basic 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 pkb, i.e.

$$pkb = -\log kb$$

For ammonia and methyl amine, the pkb values are

$$pk_{NH_3} = 4.76 \quad ; \quad pk_{CH_3NH_2} = 3.38$$

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 electron attracted by s-orbitals of hydrogen atoms where as in CH_3NH_2, sp^3—orbital of carbon pushes electrons towards nitrogen.

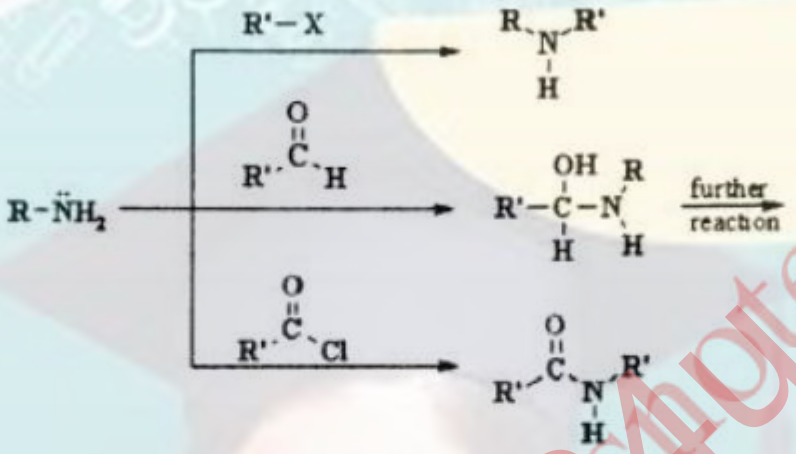
Therefore, the pair of electron on nitrogen is relatively more available in methyl amine than in ammonia. The methyl ammonium ion, $CH_3\overset{+}{N}H_3$ is stabilized due to electron donating inductive effect of the methyl group. On the other hand, NH_4^+ ion is not stabilized by hydrogen atoms. Both 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,"

(Nucleophile) (Electrophile)

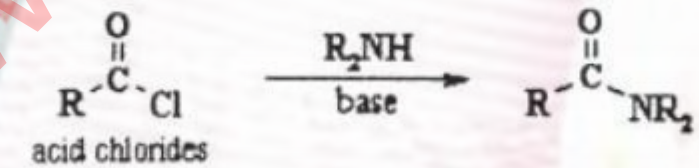
$R_2NH_2^+$ loses a proton with a base to give a free amine.

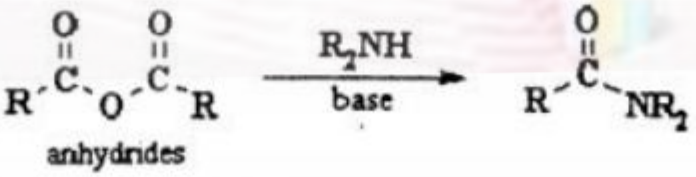
2) Reactions of Primary Amines with Aldehydes and Ketones

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.

$$RNH_2 + HNO_2 \longrightarrow \underset{\text{diazonium ion}}{R-\overset{+}{N}\equiv N} + {}^{-}OH + H_2O$$

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

$$CH_3CH_2-\overset{+}{N}\equiv N \longrightarrow N_2 + \left[CH_3\dot{C}H_2\right] \xrightarrow{H_2O} CH_3CH_2OH + H^+$$

ethyldiazonium ion

$$\left[CH_3\dot{C}H_2\right] \longrightarrow CH_2{=}CH_2 + H^+$$

When the group is attached to a benzene ring, through, the ion is stabilized to some extent by the delocalized electron of the ring. The benzenediazonium ion is therefore much more stable than its aliphatic counterparts. Nevertheless, it decomposes readily above 10°C.

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**.

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) E_1 and E_2
   b) E_2 and S_N2
   c) E_1 and S_N2
   d) E_1 and S_N1

4) **The rate of E_1 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

EXERCISE

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

1) The molecule of ethane posses which hybridization.
   a) Sp^3 b) Sp^2 c) Sp d) sp^2d

2) The Sp^3 hyrid orbitals are oriented in space at one angle.
   a) 109.5° b) 180° c) 100° d) 120°

3) The geometry of acetylene is,
   a) angular b) bent c) trigonal d) linear

4) Which reaction is used as test for the presence of alkane;
   a) reaction of cold diluted alkaline $KMnO_4$
   b) combustion
   c) polymerisation
   d) catalytic hydrogenation

5) The general formula of alkane is
   a) CnH_{2n+2} b) C_nH_n c) CnH_2n d) CnH_{2n-2}

6) Sodalime is:
   a) NaOH b) KOH
   c) Mixture of Na & Ca hydroxide d) CaO and NaOH

7) The marsh gas is:
   a) Ethane b) Methane c) Propane d) Butane

8) Acidic hydrogen is present:
   a) Acetylene b) Ethane c) Benzene d) Ethene

9) The benzene molecule contains:
   a) three double bonds b) two double bonds
   c) one double bond d) delocalized

10) The electrophile in aromatic sulphonation is:
   a) H_2SO_4 b) HSO^-_4 c) SO_3 d) SO^-_4

11) The conversion of n – hexane into benzene by heating in the presence of pt is called:
   a) isomerization b) aromatization c) dealkylation d) rearrangement

12) Catalyst used for friedal craft's reaction is:
   a) HNO_3 b) $AlCl_3$ c) $BeCl_3$ d) NaCl

13) Benzene cannot undergo:
   a) Elimination b) Subsitution c) Oxidation d) Addition

14) Shap of benzene molecule is:
   a) pyramidal b) linear planer c) trigonal d) hyxagonal planer

15) In which one of the following compounds the benzene ring is isolated:
a) Naphtalene b) Anthracene
c) Phenanthrene d) Diphenyl methane

16) Two compounds have the same composition and also have the same atoms attached to the same atoms, although with different orientations in space. These compounds are:
a) identical b) position isomer c) structural d) stereoisomerism

17) The isomers of a substance must have:
a) same chemical properties b) same molecular weight
c) same structural formula d) same functional groups

18) Ethanol and dimethyl ether are best considered.
a) structural isomers b) stereoisomers
c) enantiomers d) diastereomers

19) Alkanes show geo-metrical isomers due to:
a) asymmetry
b) rotation around a single bond
c) Resonance
d) Restricted rotation around a double bond

20) A molecule is said to be chiral:
a) If is contains plane of symmetry
b) If it contains center of symmetry
c) If it cannot be superimposed to its mirror image
d) If it can be superimposed on its mirror image

21) Geomatrical isomerism is shown by:
a) Lactic acid b) maleic acid
c) 1 - brtene d) 1, 1 dichloroethylene

22) Which of the following statements is false regarding chiral compounds:
a) rotate the plane of polarized light b) have cis and trans isomers
c) exist as enantiomers d) can be detected with a polarimeter

23) An optically active compound:
a) must contain at least four carbon
b) when in soluble rotate the plane of polarized light
c) must always contains an asymmetric carbon atom
d) in solution always give a negative reading in polarimeter

24) Plane polarized light is affected by:
a) identical molecules b) all polymers
c) chiral molecules d) All biomolecules

25) It is possible to distinguish between optical isomers.
a) by using chemical tests b) by mass spectrometry
c) by I R spectroscopy d) by polarimetry

Answer

1)	a)	2)	a)	3)	d)	4)	a)	5)	a)
6)	d)	7)	b)	8)	a)	9)	a)	10)	c)
11)	b)	12)	b)	13)	a)	14)	d)	15)	d)
16)	d)	17)	b)	18)	a)	19)	b)	20)	c)
21)	b)	22)	b)	23)	d)	24)	c)	25)	d)

Q2. Give short answers of the following questions.

Q1. Why carbon is sp^3 hybridized in the compounds?

Answer

The electronic configuration of c in ground state is

C = 6 – $\uparrow\downarrow$ 1s $\uparrow\downarrow$ 2s $\uparrow$ 2px $\uparrow$ 2py 2pz and in excited state, it is

C = 6 = $\uparrow$ 1s $\uparrow$ 2s $\uparrow$ 2px $\uparrow$ 2py $\uparrow$ 2pz

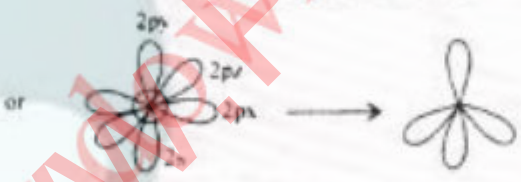
In alkanes and in single bonded carbon compounds every carbon atom in its second shell i.e in 2s, 2p, 2py, 2pz contains one unpaired electron in each orbital when hydrogen atoms or other atoms which one more than carbon atoms surrounds the central atom these four orbitals of 2nd shell mix with each other and produce four equal energy sp3 orbitals. These orbitals stay at equal positions and form tetrahedral shaped compounds.

i.e.

C = 6 = $\uparrow$ 1s | $\uparrow$ 2s $\uparrow$ 2px $\uparrow$ 2py $\uparrow$ 2pz

Four, sp^3 hybrid orbitals

or



Q2. How is pi-bond formed in alkenes and alkynes?

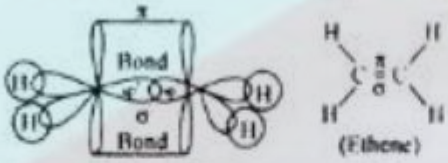
Answer

In alkenes one s and twp p-orbitals mix and produce there sp2 hybridized orbitals – leaving one p – orbital unhybridized two such atoms having one unhybridized p-orbital when some closer to each other two sp2 orbitals of two carbon atoms overlap each other and form a sigma bond. Than unhybridized two p – orbitals of two carbon atom overlap over each other and form a pi-bond.

i.e in ground state C = 6 = 1s 2s 2px 2py 2pz

In excited state C = 6 = 1s 2s 2px 2py 2pz

Three sp^2



In alkynes

In alkynes in 2nd – shell of carbon (initsexted – state) one exited atom mixes with one – p orbital and produce two sp hybridized orbitals leaving two p – orbitals unhybridized in each carbon. When thse two carbon atoms come closer to each other sp of one atom overlaps on sp of other atom and there is formed one – sigma bond than two p- orbitals of one atom over lap on two p-orbitals other carbon atom and form two pi-bonds. As a results an alkyne is formed.

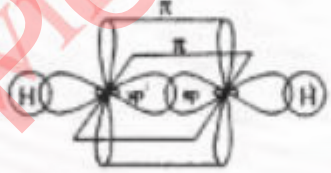
For example ethyne ($C_2 H_2$)

i.e in ground state

i.e in ground state C = 6 = 1s 2s 2px 2py 2pz

and in excited state C = 6 = 1s 2s 2px 2py 2pz

Two sp



H – C ≡ C – H

(one σ and two π - bonds)

Q3. What is cis-trans isomerism?

Answer

Please see answer of Q42 of chapter notes.

Q4. Why alkanes are relatively chemically inert?

Answer

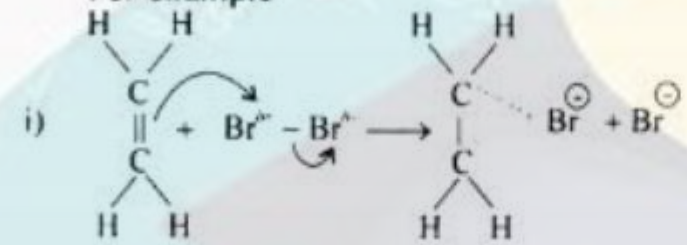
In alkanes there is sp^3 orbital hybridization in each carbon. One sp3 orbital of when overlaps on sp^3 orbitals of adjacent atom there is formed a very strong sigma bond of very low energy such a sigma bond is very strong and may only be decomposed at very high energy. That is why alkanes one very stable and least reactive at room temperature.

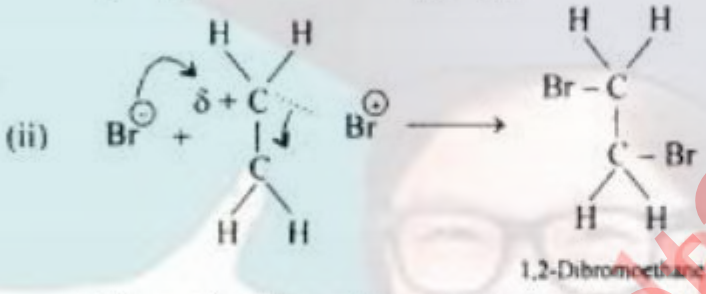
Q5. Alkenes usually undergo addition reactions while alkanes do not why?

Answer

In alkenes there is one exposed pi-bond which is very reactive. Because this exposed pi-bond may attack at positive or partial positive charge of an electrophile.

For example





1,2-Dibromoethane

Whereas in alkanes there are strong low energy sigma bonds which are nearly inert and do not take part in any reactions easily.

Q6. What is stereoisomerism?

Answer

Please see answer of short questions of Q44 (b) of chapter notes.

Q7. How optical isomers arise?

Answer

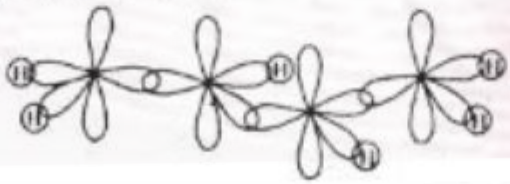
Please see answer of short questions of Q44 (d) of chapter notes.

Q8. How are conjugated bonds formed?

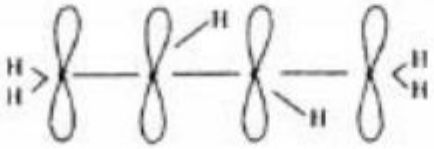
Answer

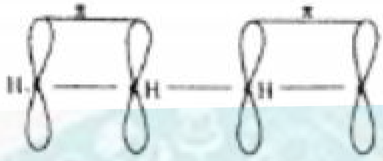
In a molecule in which there are left unhbridized p – orbitals on adjacent atleast three c – atoms the molecule is called a conjugated molecule. These adjacent p – orbitals are responsible for resonance.

For example; 1,3-Butadiene



O = C – atoms





$$\overset{\ominus}{C}H_2=CH-CH=CH_2 \leftrightarrow CH_2-CH=CH-\overset{\ominus}{C}H_2$$

Q9. Why alkenes are more reactive than alkynes?

Answer

In alkenes there is one pi-bond which is exposed and may attack at any positive or partial positive charge therefore very reactive.

Whereas i alkynes there are two pi-bonds which form a new cylindrical shaped orbital which is lesser reactive as compared to alkenes.

Q10. Justify the given order of reactivity?

Answer

Alkenes have exposed pi-bond which may attack at any electrophilic center. Therefore it is most reactive.

In alkynes there are two pi-bonds around one sigma bond these two pi-bonds form a cylindrical shaped orbital which is stable and lesser reactive.

Whereas in alkanes there are c – c very stable low energy sigma – bonds which are least reactive.

Q11. What is meant by dehydration?

Answer

Dehydration means removal of water dehydration of alcohols is a temperature dependent reaction which gives different products

For Example

$$2CH_3-CH_2-OH \xrightarrow[H_2SO_4]{140^\circ C} CH_3-CH_2-O-CH_2-CH_3+H_2O$$

(Ether)

$$2CH_3-\underset{\underset{OH}{|}}{CH_2} \xrightarrow[H_2SO_4]{180^\circ C} CH_2=CH_2+H_2O$$

(Alkene)

Q12. What are polymerization reactions?

Answer

(Poly = more than one f meros = pieces)

Attachment of large number of small molecules to give a bigger molecule is called polymerization type of product of a polymerization of alkenes and alkynes depend upon the condition of the reaction like temperature, pressure and catalyst.

For Example

$$3H-C\equiv C-H \xrightarrow[300\ ^{\circ}C]{Cu\text{ - Tube}} \text{Benzene}$$

$$3H-C\equiv C-H \xrightarrow[Cu_2Cl_2]{NH_4Cl} CH_2=CH-C\equiv C-CH=CH_2$$

Divinyl Acetylene

$$4H-C\equiv C-H \xrightarrow[\text{i.e. Nickel carbonyl}]{Ni(CO)_4}$$

(Cyclooctatetraene)

$$n\ CH_2=CH_2 \xrightarrow[0.1-0.2\%O_2\ (\text{traces of } O_2)]{250\ ^{\circ}C,\ 450\ atm} (CH_2-CH_2)_n$$

Polythene

Q13.How will you convert acetylene into benzene?

Answer

Conversion of acetylene into benzene

$$3H-C\equiv C-H \xrightarrow[300\ ^{\circ}C]{Cu\text{ - Tube}}$$

Benzene

Q14.What is resonance?

Answer

Shifting of pi-electrons from one position to another position is called resonance.

For example: In 1, 3 – butadiene

$$CH_2=CH-CH=CH_2$$

$$\leftrightarrow \overset{\oplus}{C}H_2-CH=CH-\overset{\ominus}{C}H_2$$

$$\leftrightarrow \overset{\ominus}{C}H_2-CH=CH-\overset{\oplus}{C}H_2$$

Q15.What is resonance energy?

Answer

Resonance Energy

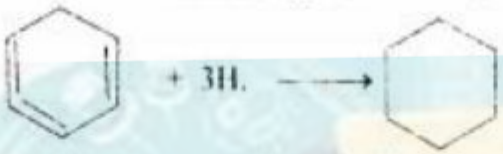
On hydrogenation of a conjugated molecule the difference between obtained actual energy and expected energy is called resonance energy.

For Example: heat of hydrogenation of cyclohexene is – 120 KJ mole^{-1}

i.e.

$$+ H_2 \longrightarrow -120\ KJ\ mol^{-1}$$

Now, of we consider benzene as cyclohexatriene, and calculate expected energy.



$$+ 3H_2 \longrightarrow \qquad -120 \times 3x$$

Expected Energy = -360

But actual obtained energy = -208

Difference of Energy (Resonance Energy) = -152

The difference of these two energies i.e. – 152KJ mole^{-1} is called resonance energy.

Q3. Give detail answers of the following questions.

Q1. What is isomerism? Explain different types of isomerism?

Answer

Please see answer of question 38 and 39 of this chapter.

Q2.a)How will you prepare 1 – butane from?

i) An alkylhalide **ii) Alcohols**

iii) Electrolysis of salt **iv) Vic - dihalides**

b) What products is formed when n-propane under go following reactions?

i) Combustion **ii) Nitration**

Answer a)

i) Preparation of 1 – butane from alkyl halide

$$CH_3-CH_2-CH_2-CH_2 + KOH \xrightarrow{(alc)} CH_2=CH-CH_2-CH_3 + Kbr + H_2O$$

$CH_2-CH_2-CH_2-CH_2$
|
Br
(1-bromobutane)

ii) 1 – butene from an alcohol

$$CH_3-CH_2-CH_2-CH_3 \xrightarrow[175°C]{75\%H_2SO_4} CH_2=CH-CH_2-CH_3 + H_2O$$

$CH_3-CH_2-CH_2-CH_3$
|
OH

iii) 1 – butene from Electrolysis of salt

$$\begin{array}{l} CH_2-COONa \\ | \\ CH-COONa \\ | \\ CH_2 \\ | \\ CH_3 \end{array} + 2HO \xrightarrow[H_2O]{Elec} \begin{array}{l} CH_2 \\ \| \\ CH \\ | \\ CH_2 \\ | \\ CH_3 \end{array} \begin{array}{l} \\ \\ + 2NaOH \\ \\ + 2CO_2 \\ \\ + H_2 \end{array}$$

sodium salt of 2 - ethyl butanedioic acid

iv) **1 – butane from vic – dihalide**

$$CH_2-CH_2-CH_2-CH_3 \xrightarrow[(alc)]{+2KOH} CH_2=CH-CH_2-CH_3 + 2KCl + 2H_2O$$

(Cl, Cl)

Answer b)

i – Combustion of n – propane

$$CH_3-CH_2-CH_3 + HNO_3 \xrightarrow[\Delta]{H_2SO_4} CH_3-CH_2-CH_2-NO_2 + CH_3-CH_2-NO_2 + CH_3-NO_2 + H_2O$$

These all are possible products present as mixture

Q3.a)When ethane reacts with Cl_2 in UV light the mixture of products is formed. Give the detail of reaction with mechanism and all types of products.

b) A compound when treated with Zn in methanol, the alkene is formed. When alkene is ozonolysed the acetaldehyde is formed as the major products. Explain reactions, give name and structure of the compound.

Answer a)

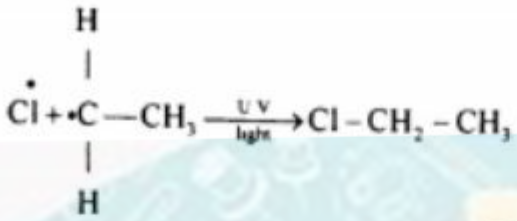
Reactions of ethane with Cl_2 in presence of UV light

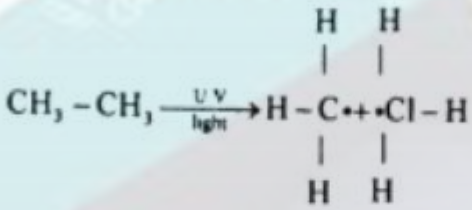
$$CH_3-CH_2-Cl \xrightarrow[light]{UV} CH_3-\underset{\displaystyle Cl}{\underset{|}{CH_2}} + CH_3-Cl + HCl$$

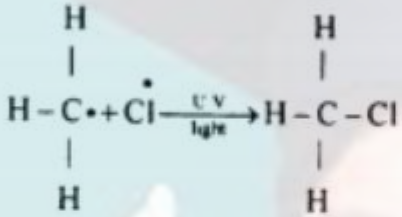
Reaction Mechanism

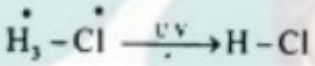
$$Cl-Cl \xrightarrow[light]{UV} Cl-Cl$$

$$H-\underset{\displaystyle H}{\underset{|}{C}}-CH_3 \xrightarrow[light]{UV} \dot{H} + \cdot\underset{\displaystyle H}{\underset{|}{C}}-CH_3$$

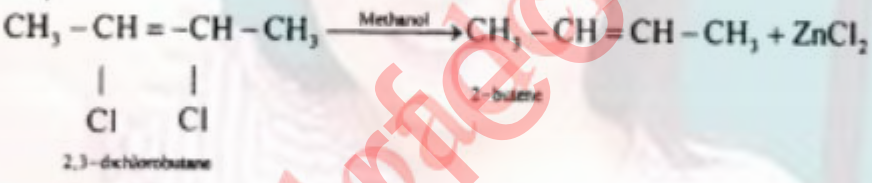


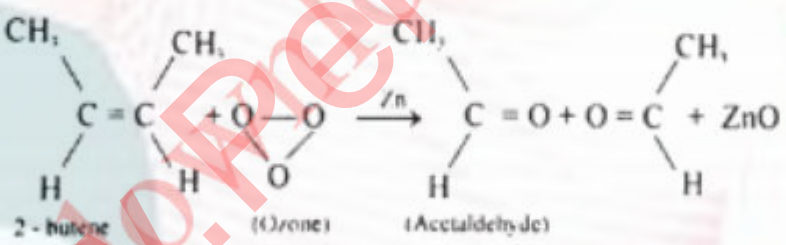






Answer b)





Q4.a)How will you prove that benzene has cyclic structure?

b)Explain the structure of benzene according to atomic orbital structure.

Answer

a) Please see answer of question 69 and of this chapter.

b) Please see answer of question 79 and of this chapter.

Q5. Explain Friedel Craft acylation and alkylation with complete mechanism.

Answer

For Friedel Craft acylation please see answer of Q80 of this chapter.

For Friedel Craft alkylation please see answer of Q79 of this chapter.

Q6. Explain the following electrophilic substitution reactions of benzene with mechanism.
i) Halogenation ii) Nitration iii) Sulphonation

Answer

I) Halogenation

Please see answer of question 73 and of this chapter.

II) Nitration

Please see answer of question 76 and of this chapter.

III) Sulphonation

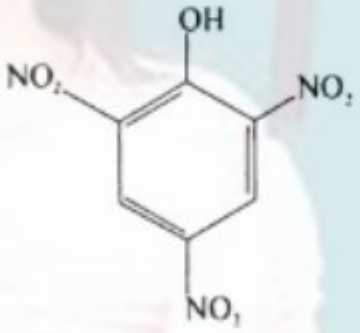
Please see answer of question 77 and of this chapter.

Q7. Write the structural formulas for the following benzene derivatives:

a) 2, 4, 6 – trinitrophenol
b) 1, 4 – dichlorobenzene
c) 2 – methylbenzene sulphonic acid
d) 2 – hydroxybenzoic acid
f) 2 – chlorophenylamine

Answer

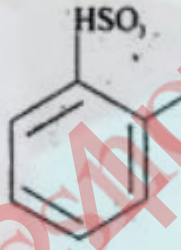
a) 2, 4, 6 – trinitriphenol



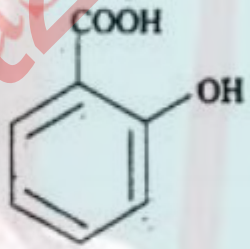
b) 1, 4 – dichlorobenzene

c) 4 – nitrophenylamine

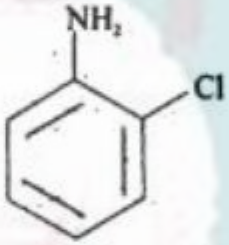
d) 2 – methyl benzene sulphuric acid



e) 2 – hydroxybenzoic acid

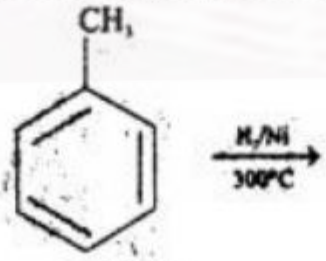


f) 2 – chlorophenylamine

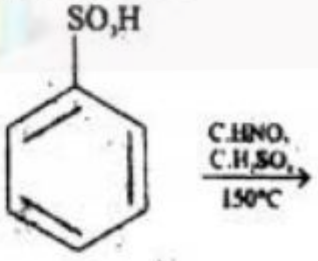


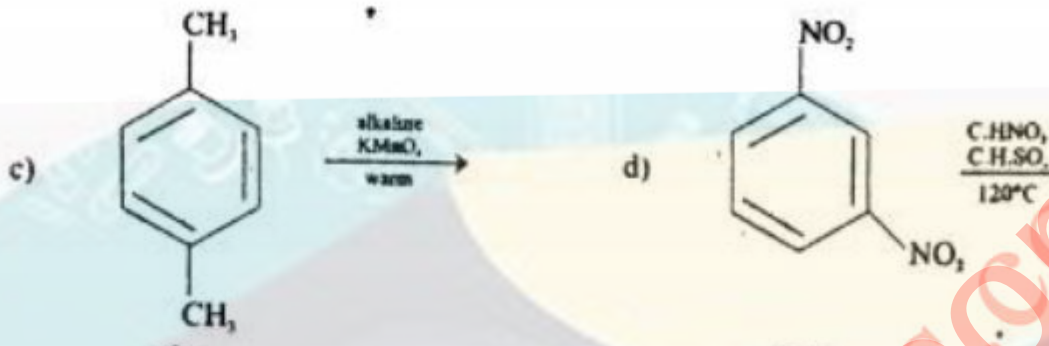
Q8. Predict the major products of the following reactions.

a)

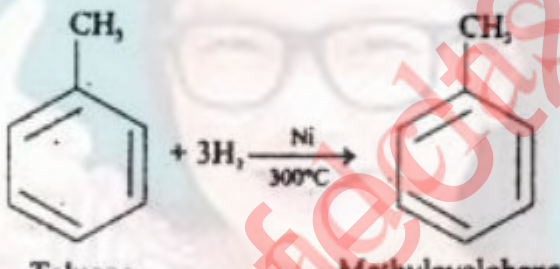


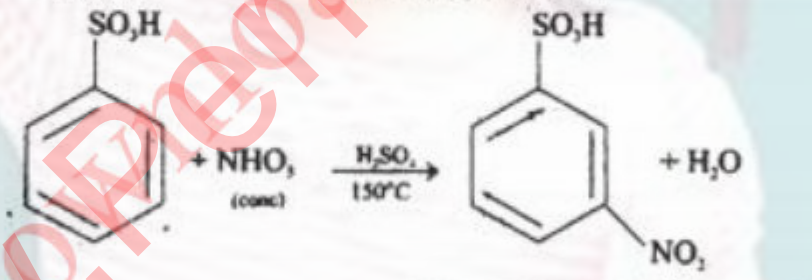
b)



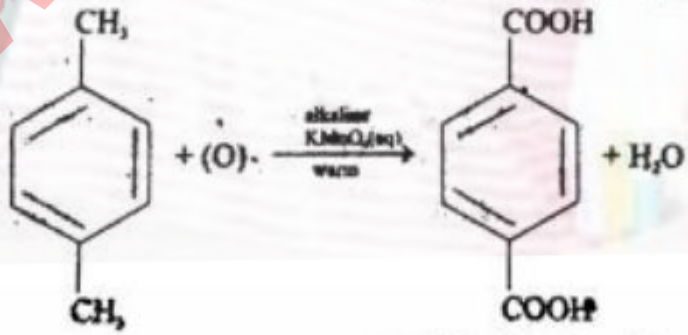


Answer



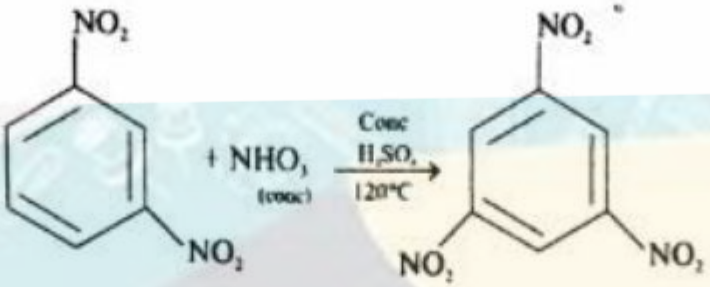


(m - nitro sulphonic benzene)

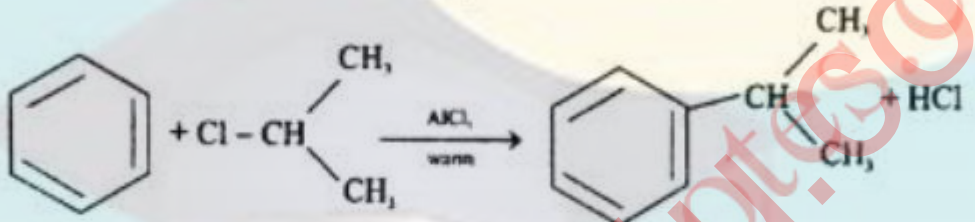


(Terephthalic acid)

d)

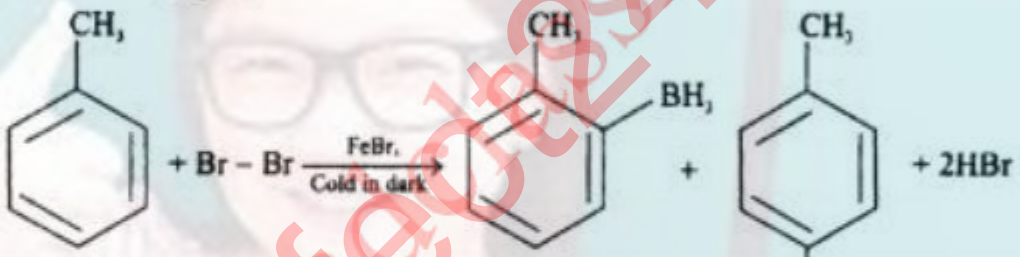


c)



Propane Isoprophyl benzene

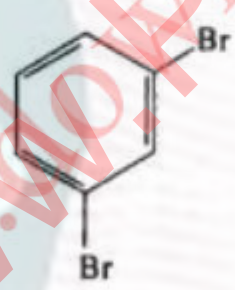
f)



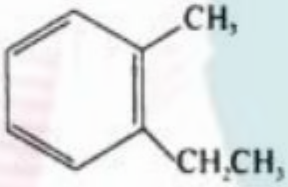
0 - bromo toluene P - bromo toluene

Q9. Name the following benzene derivatives.

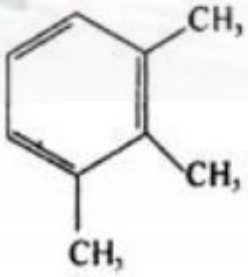
a)



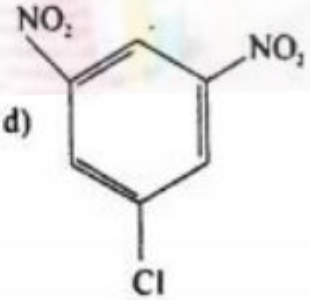
b)



c)

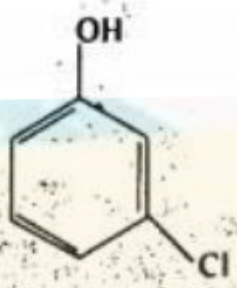


d)



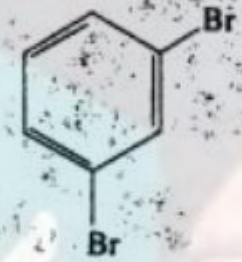
e)

f)



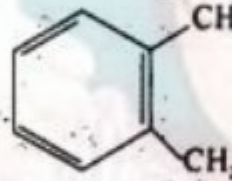
Answer

a)



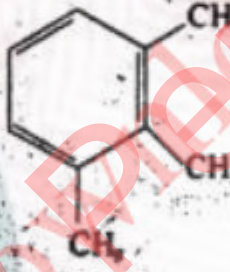
1, 3 – dibromobenzene

b)



2 – ethyltoluene

c)

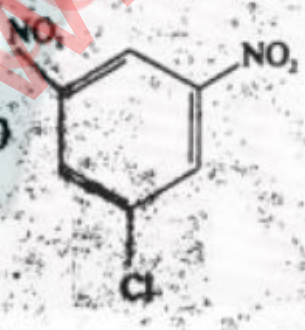


1, 2, 3 – trimethyl benzene

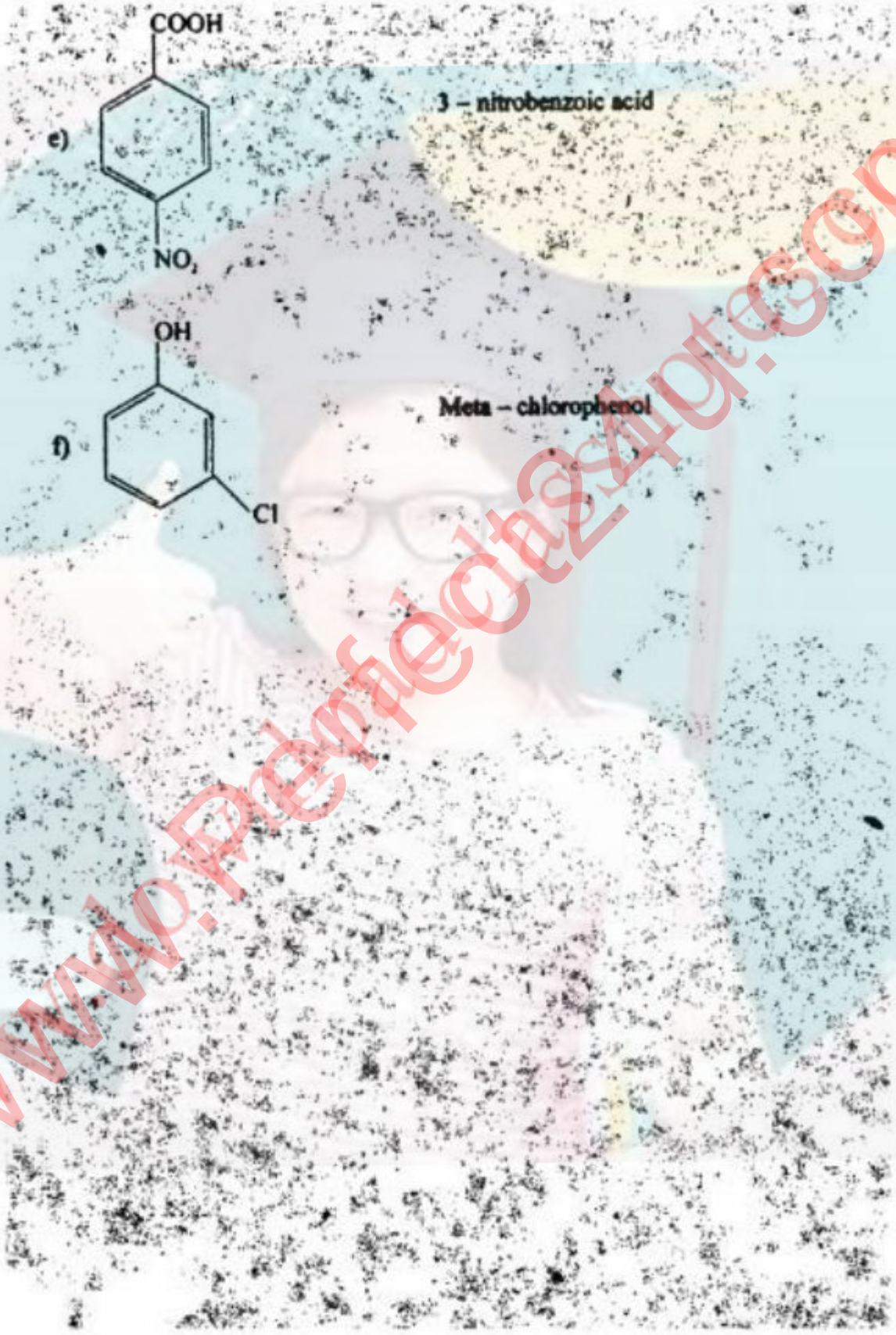
Or

2, 3 – dimethyl toluene

d)



5 – bromo – 3 – chloronitrobenzene



Give Short Answers

Q1: 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: $C^{*}H_3 - Cl$, $CH_3 - C^{*}H_2 - Cl$

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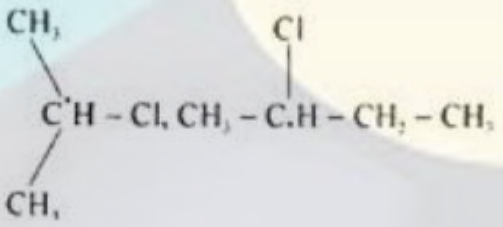
Q3: What are secondary alkyl halides? Give examples.

Answer

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

Example:



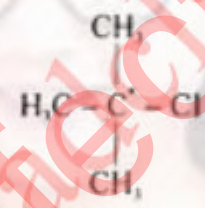
2 — Chloropropane 2 — Chlorobutane

Q4: What are tertiary alkyl halide? Give example.

Answer

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

Example:



1 — Butyl chloride

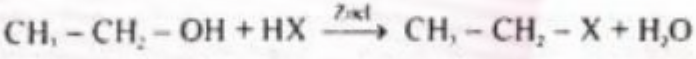
Q5: Why alkyl halides have higher melting & Boiling points compared to alkanes?

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 pllustrate the conversion of alcohols into the alkyl halides.

Answer



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 subsitution reaction".

Answer

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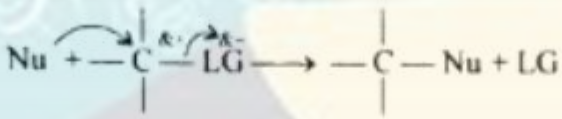
Nucleophilic subsitution reaction occure when an electron rich species, the nucleophile reacts at an alectrophilic C-atom attached to an electronegative group.

i.e



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

Answer

These are as follows

i — Formation of new s bond to the nucleophile.

ii — Breaking of the living group.

Q10: 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^- $C_2H_5O^-$, HS^-, H_2O

Q11: Define substrate?

Answer

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

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^-, I^-.etc

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

Examples: OH^-, OR, NH_2^- etc

Q14: What is SN_1 Mechanism?

Answer

It is substitution nucleophilic bimolecular two step reaction.

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

$$R^+ - Nu \xrightarrow{Fast} R - Nu$$

Q15: What is SN_2 Mechanism?

Answer

It subsitution nucleophilic bimolecular reaction which occurs in one step.

$$Nu + CH_3 - X \longrightarrow Nu - CH_3 + X$$

Q16: What are elimination reactions?

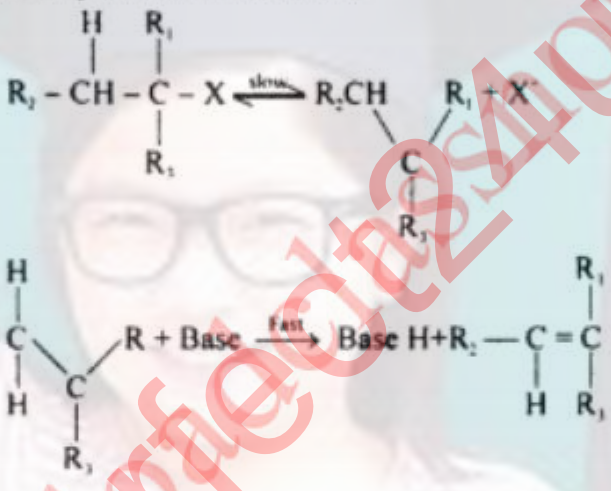
Answer

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

Q17: What is Er mechanism?

Answer

It is unimolecular two step eliminationreactions



Q18: What is Ez mechanism?

Answer

It is bimolecular one step elimination reaction

Q19: Under which condition the elimination reaction occurs?

Answer

Elimination reaction occurs only when the substance have β-hydrogen.

Q20: What is sp^3 hybridized?

Answer

The process in which three-p orbitals and one-s orbital combine together to give sp^3 hybrid orbital this is called sp^3 hybridization.

Q21: Define Bond energy?

Answer

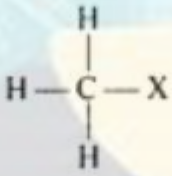
The energy which is required to form a bond is called bond energy.

Q22: What are monohaloalkanes? Give example.

Answer

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

Example:



Q23: How Grignard's reagents are prepaired?

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 Grignoral 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 N–H bond which results in formation of hydrogen bonds with other H-bonding systems.

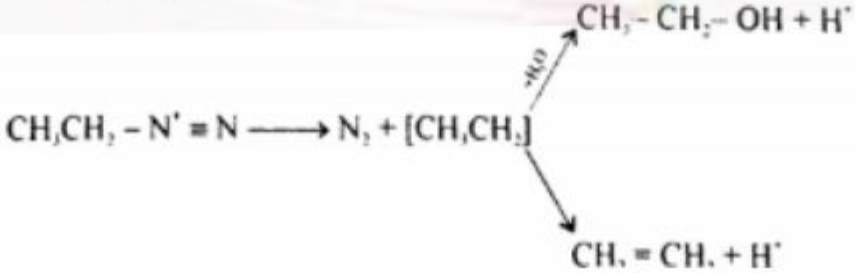
Q27: What is Diazonium salt?

Answer

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

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

The diazinium 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 antifungle 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.