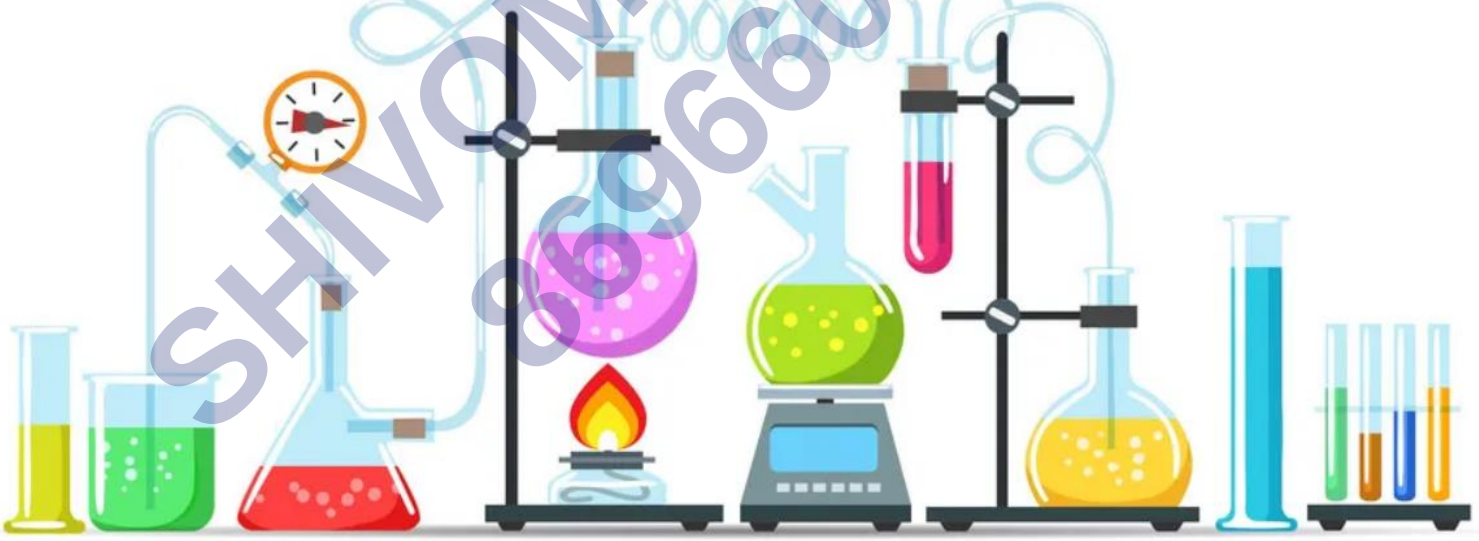
CHEMISTRY

CHAPTER 12: ORGANIC CHEMISTRY SOME BASICPRINCIPLES AND TECHNIQUES



ORGANIC CHEMISTRY SOME BASICPRINCIPLES AND TECHNIQUES

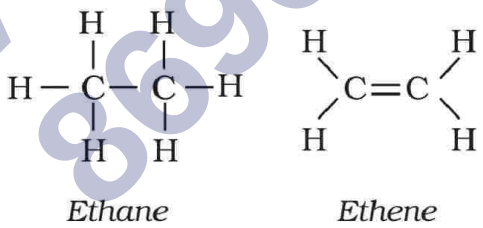
Introduction

In this chapter, we shall discuss some basic principles and techniques of analysis needed for understanding the formation and properties of organic compounds. Organic compounds are essential for existence and maintenance of life on earth. These include complex molecules like (DNA) which carry genetic information and proteins which is building blocks of life. Organic compounds also play an important role in material used in daily life such as cloths, fuel, dyes, and medicines etc.

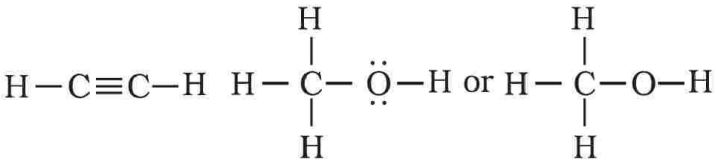
Structural Representations of Organic Compounds

Structural Formulas

The Lewis structures can be simplified by representing the two electron covalent bonds by a dash (–). In this representation, a single bond is represented by a single dash (–), a double bond by a double dash (=) and a triple bond by a triple dash (≡). The lone pair on an atom may or may not be shown. This representation is called structural formula.



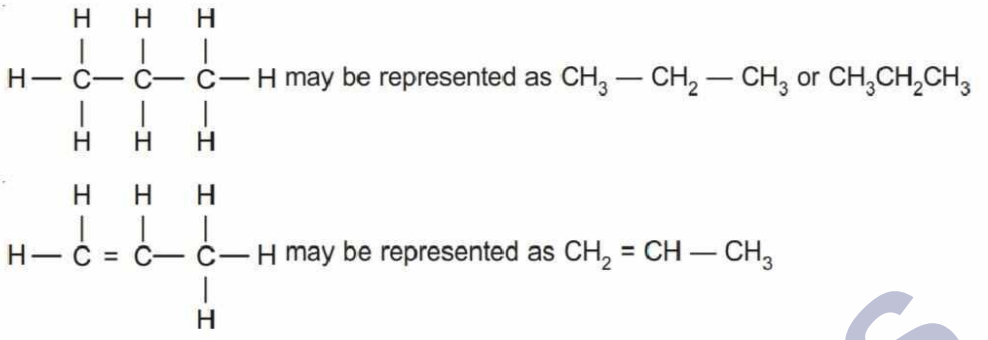
Ethane *Ethene*



Ethyne *Methanol*

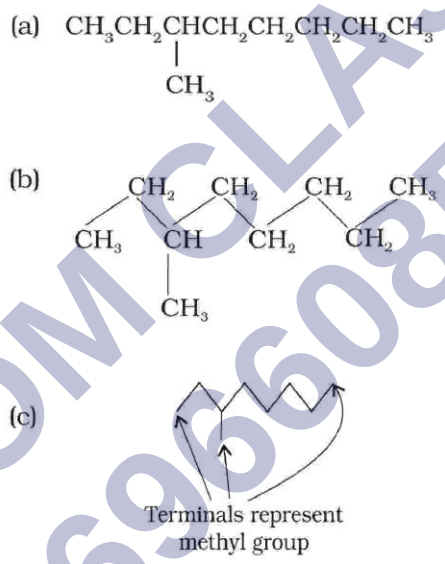
Condensed Formulas

In this formula, the arrangement of atoms are shown but the bonds between may be omitted and the number of identical groups attached to an atom are indicated by a subscript.

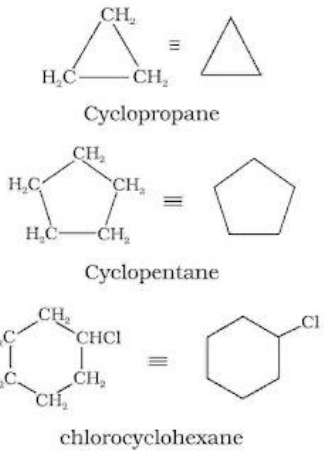


Condensed Formulas

In this representation, the carbon and hydrogen atoms are not shown and the lines between carbon-carbon bonds are shown in a zig-zag manner.

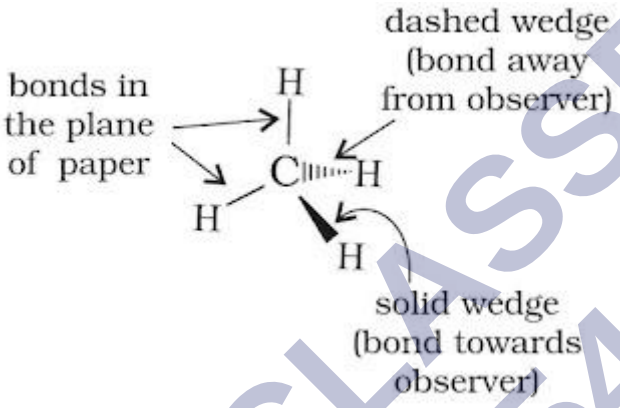


In cyclic compounds, the bond-line formulas may be given as follows:



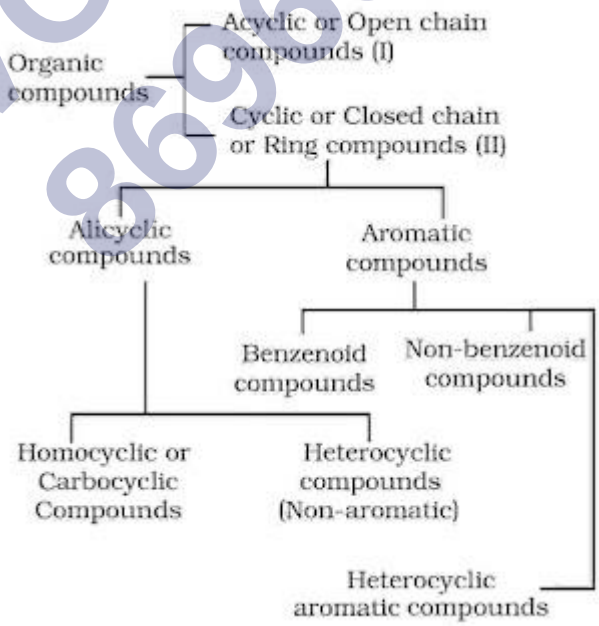
Three-dimensional representation of organic molecules

The three-dimensional (3-D) structure of organic molecules can be represented on paper by using certain conventions. In these formulae, the thick solid (or heavy) line or the solid wedge indicates a bond lying above the plane of the paper and projecting towards the observer while a dashed wedge is used to represent a bond lying below the plane of the paper and projecting away from the observer.



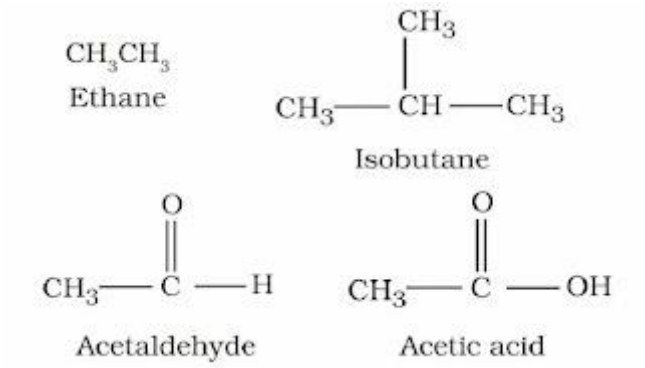
Classification of Organic Compounds

On the basis of their structures, organic compounds are broadly classified as follows:



Open Chain Compounds

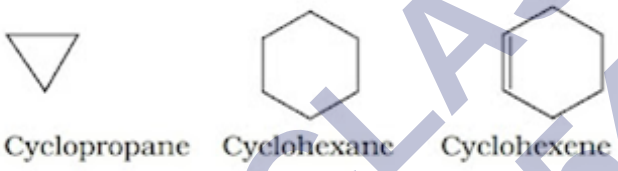
These compounds contain open chains of carbon atoms in their molecules. The carbon chains may be either straight chains or branched chains. They are also called aliphatic compounds.



Closed Chain or Ring Compounds

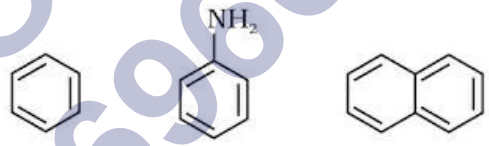
These compounds contain chains or rings of atoms in their molecules.

Alicyclic Compounds: These compounds contain a ring of three or more carbon atoms in them. They resemble aliphatic compounds in many of their properties.



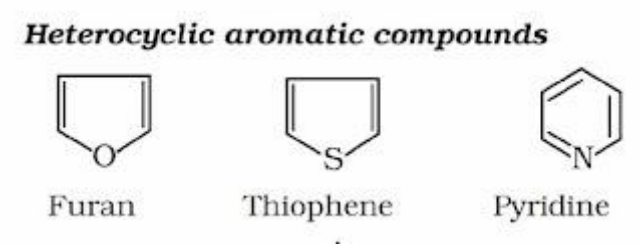
Aromatic Compounds: These have a cyclic system containing at last one benzene ring. The parent member of the family is called benzene. Benzene has a homocyclic hexagonal ring of six carbon atoms with three double bonds in the alternate positions.

Benzenoid aromatic compounds

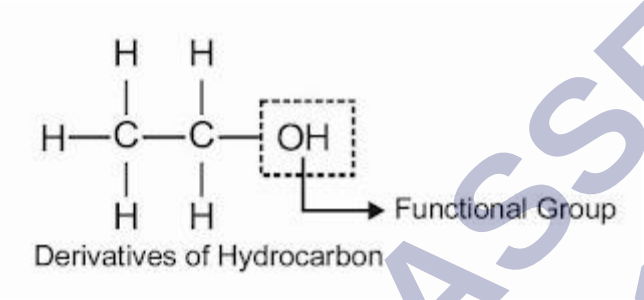


Non-benzenoid compound

Heterocyclic Compounds: In these compounds, the ring contains one or more atoms of either nitrogen, oxygen or sulphur in addition to carbon atoms. The atom other than carbon (such as N, O, S) present in the ring is called hetero atoms.



Functional Groups: An atom or group of atoms which largely determines the properties of the organic compounds particularly the chemical properties.



Homologous Series: Homologous series may be defined as "a series of similarly constituted compounds in which the members possess the same functional group and have similar chemical characteristics". The two consecutive members differ in their molecular formula by – CH_2– group.

1. CH_3OH - Methyl alcohol
2. C_2H_5OH - Ethyl alcohol
3. C_3H_7OH - Propyl alcohol
4. C_4H_9OH - Butyl alcohol
5. $C_5H_{11}OH$ - Pentyl alcohol
6. $C_6H_{13}OH$ - Hexyl alcohol

Nomenclature of Organic Compounds

The term 'nomenclature' means the system of naming of organic compounds. There are two systems of nomenclature:

1. **Trivial or Common System**

   In this nomenclature, the names of organic compounds were assigned based on their source of origin or certain properties. For instance, citric acid got its name from the source (citrus fruits) from which it was first isolated. Formic acid was named so as it was first obtained from red ant. In Latin ant word is formica.

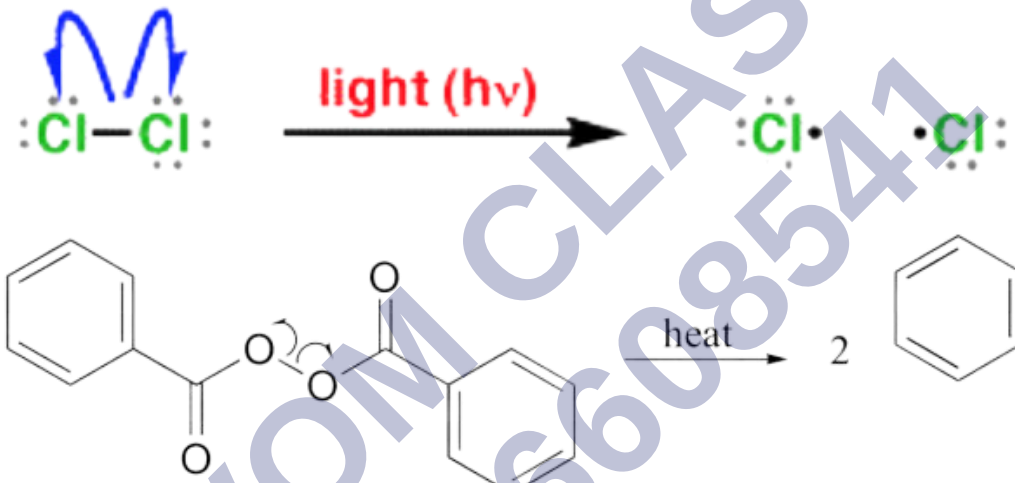
2. **IUPAC System of Nomenclature**

A systematic method of naming has been developed and is known as the IUPAC (International Union of Pure and Applied Chemistry) system of nomenclature. In this systematic nomenclature, the names are correlated with the structure such that the reader or listener can deduce the structure from the name.

Free Radicals

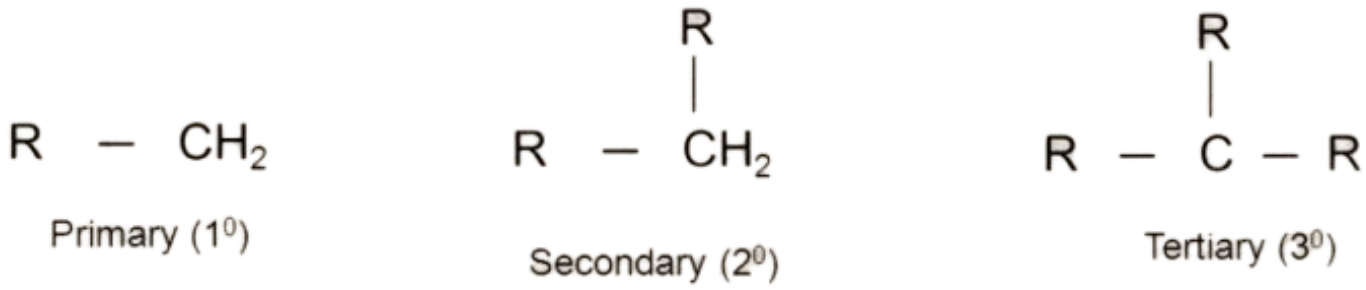
Free Radical

A free radical may be defined as an atom or a group having an odd or unpaired electron.These are generally produced by homolytic cleavage of a covalent bond.



Classification of Free Radicals

Free radicals are also classified as primary (1°), secondary (2°) and tertiary (3°) according as the carbon carrying the unpaired electron is primary, secondary and tertiary.

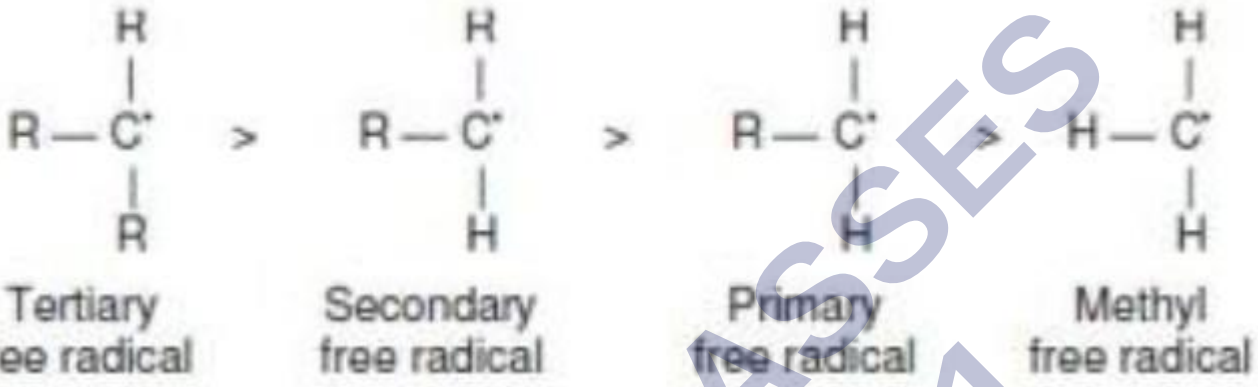


Stability of Free Radicals

The order of stability of free radicals is the same as that of carbocations i.e. 3° >2° >1°

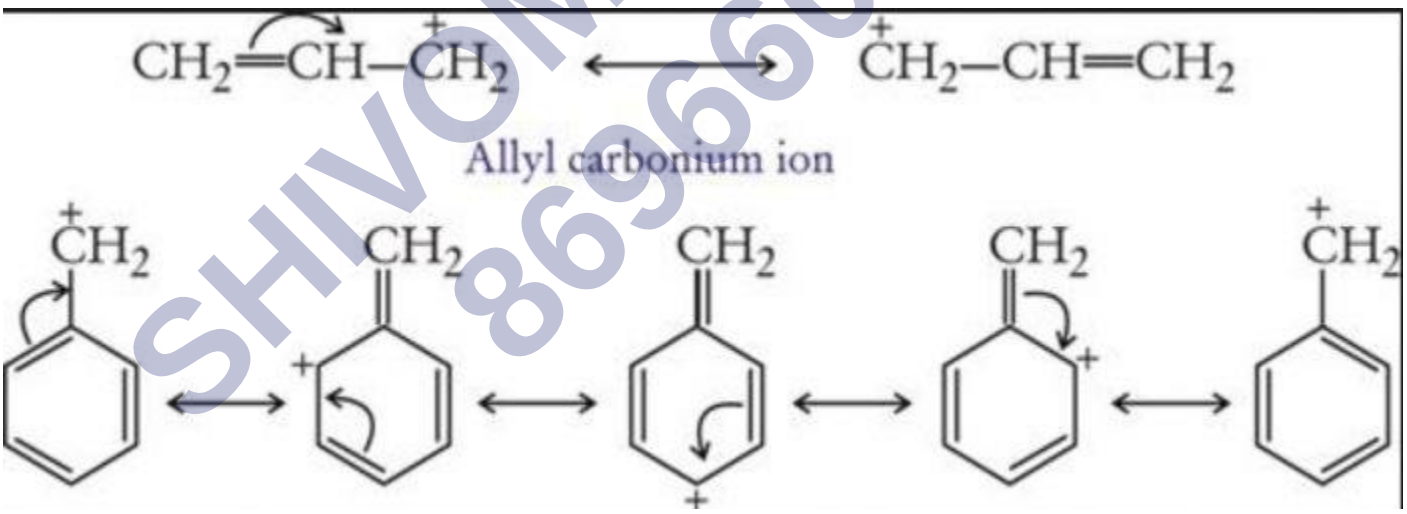
This order of stability can be explained on the basis of hyperconjugation.

Greater the number of alkyl groups attached to the carbon atom carrying the odd electrons, greater is the delocalization of the odd electrons and hence more stable is the alkyl free radical.



Stability of free radical

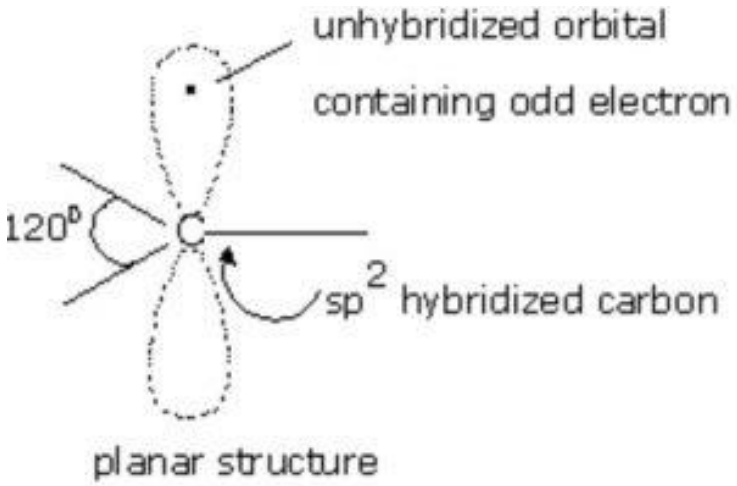
Allyl and benzyl free radicals are stabilized by resonance.



Greater the number of phenyl groups more stable is the free radical.

Free radicals are also very short-lived highly reactive chemical species because of the strong tendency of the carbon atom carrying the odd electron to acquire one more electron to complete its octet.

Orbital structure of Free Radicals



Alkyl free radicals are planar chemical species.In free radicals, the unhybridized p-orbital contains the odd electron.

Like carbanions , free radicals can also assume pyramidal shape since the energy difference between planar and pyramidal shape is not much.

Stereoisomerism

Isomers which have same structural formula but have different relative arrangement or atoms or groups in space are called stereoisomers and the phenomenon is called stereoisomerism.

cis-trans isomerism is an example of stereoisomerism.

cis-trans isomers

Due to π-bonding between the two carbon atoms, the rotation around carbon-carbon double bond is prohibited and hence the geometry of the atoms or groups attached to the carbon atoms gets fixed in space.

Stereoisomerism is also called geometrical isomerism.

Steric Hindrance

If two non-bonded atoms or groups in an organic molecule are held together at a distance equal to or less than the sum of their van der waal radii, then they repel each other due to spatial crowding.This repulsion is referred to as steric hindrance or steric strain or van der waal strains.

Molecules which possess steric strain are relatively less stable as compared to those having no steric strain.

For Example: Cis-but-2-ene has steric hindrance and hence is less stable as compared

to trans-but-2-ene which has no steric hindrance.

As the size of the atoms around a bulky atom increases, the steric hindrance increases accordingly.

Summary-

1. **Condensed Structural Formula:** The structural formulae obtained by omitting some or all the covalent bonds and by indicating the number of identical groups attached to an atom by subscript is called condensed structural formula.
2. **Bond-line Structural Formula:** In this formula of organic compounds, carbon and hydrogen atoms are not shown and line representing C –C bonds and drawn in zig-zag fashion. The only atoms specifically written are those that are neither nor hydrogen bonded to carbon.
3. **Cyclic Compounds:** These are compounds in which carbon atoms are joined in rings i.e., they are closed chain compounds.
4. **Aromatic Compounds:** Benzene and its derivatives are called aromatic compounds.
5. Functional group: Functional group is an atom or group of atoms or reactive part of the compound which determines physical and chemical properties of compounds.
6. **Homologous Series:** Homologous series is a series of compounds which has same functional group same general formula and show gradation in physical and chemical properties of compounds.
7. **Isomerism:** The phenomenon of existence of two or more compounds possessing the same formula but different structural formula and different physical and chemical properties are called isomerism.
8. **Structural Isomerism:** Compounds having the same molecular formula but different structures are classified as structural isomers. Chain Isomerism: The isomers, which differ in carbon atom chain, are called chain isomers and this phenomenon is called chain isomerisms.
9. **Position Isomerism:** The isomers, which differ in position of substituent or functional groups are called position isomers and this phenomenon is called position isomerism.
10. **Functional Isomerism:** Those isomers, which differ in functional groups are called functional isomers and this phenomenon is called functional isomerism.
11. **Metamerism:** Those isomers, which differ in alkyl group attached with the di or tri valent atom of functional group. These are called metamers and this phenomenon is called metamerism.
12. **Stereoisomerism:** Those compounds that have the same composition and sequence of covalent bond but differ in relative positions of their atoms or groups in space.

13. **Free Radical:** An atom or group of atoms containing odd unpaired electrons in excited state is known as free radical.

Class : 11th Chemistry
Chapter- 12: Organic Chemistry – Some Basic Principles & Techniques

Organic Chemistry – Some Basic Principles & Techniques

Characteristics of Bonds:
- Electron charge cloud is located above and below plane of bonding atoms.
- Provide most reactive centres.

Hyperconjugation
Delocalisation of electrons of C-H bond of an alkyl group directly attached an atom of unsaturated system

Resonance Effect Polarity
produced in the molecule by interaction of bonds or between
a bond and lone pair of electrons of a adjacent atom.

Electromeric Effect
Complete transfer of a shared pair of
electrons to one of atoms joined by a multiple bond on the demand of an attacking agent

Heterolytic Cleavage

Homolytic Cleavage

- Same Positions of nuclei.
- Same number of unpaired electrons. Example: Benzene

Fission of Covalent Bond

Nucleophile (Nucleus seeking)

Resonance Structure

Inductive Effect
Polarisation of - bond caused by polarisation of adjacent - bond.

Electrophile (Electron seeking)

Organic molecule —Attacking reagent→ [Intermediate] → Product (s)
[Intermediate] → Byproducts

Electron movement shown by curved-arrow notation Organic Reaction Mechanism

Nomenclature
(i) Identify longest carbon chain in the molecule.
(ii) Numbering is done so that branched C atoms get the lowest possible numbers
(iii) Name of alkyl, group is prefixed to parent followed by position of substituent
(iv) Lowest number is given to one coming first alphabetically.
(v) C atom attached to root is numbered first.
Functional Group : atom/ group of atoms responsible for chemical properties of organic compounds.
Homologous Series : group/series containing a characteristic functional group.

Qualitative Direction of Elements
(i) **C and H:** By heating with copper (II) oxide.
(ii) **Nitrogen:** Sodium fusion extract is boiled with iron (II) sulphate, then acidified with conc. H_2SO_4
(iii) **Sulphur:** Sodium fusion extract is acidified with acetic acid and lead acetate is added.
(iv) **Halogens:** Sodium fusion extract is acidified with silver nitrate.
(v) **Phosphorus:** Compound is heated with an oxidising agent.

Quantitative Analysis
C& H: H_2O and CO_2 formed on oxidation are absorbed in and anhydrous $CaCl_2$ and KOH solutions respectively contained
in U tubes.
Nitrogen: Dumas method and Kjeldahl's method
Halogen: Carius method
Sulphur: Carius method
Phosphorus: Known mass is heated with fuming HNO_3 and oxidised to phosphoric acid.

3D Representation: using solid(▬) and dashed(▮▮▮)
(i)Complete ethene
(ii)Condensed $H_2C{=}CH_2$ ethene
(iii)Bond-line 2-brome butane

Structural Formulas

Hybridisation
Influences bond length and bond enthalpy

Shape of C Compound

Types of Organic Reaction:
Substitution
Addition
Elimination
Rearrangement

Isomerism: Compound with same molecular formula but different Structure

Classification of Organic Compound

Stereoisomerism:
similar constitution, different in relative position of atoms /groups

Structural:
same molecular formula but different structures

Acyclic/Open Chain: Consist of straight or

Cyclic/Closed Chain/ring: Carbon atoms in a

Optical

Geometrical

Functional: group different functional group

Chain:
same molecular formula, different

Position:
different position of substituent atom /functional group

Metamerism:
different alkyl chain on either side of functional group

Heterocyclic: Atoms other than C are also present

Homocyclic/ carbocyclic: Only C atoms are present.

Alicyclic: Both aliphatic and cyclic

Aromatic: Contains conjugated planar ring system

Example: Benzene, Aniline, Naphthalene

Non benzenoid Example: Tropolene

Methods of Purification of Organic Compund
(i) Sublimation:
* **Principle:** On heating, some solid substances change from solid to vapour directly. Used to separate sublimable compounds from non-sublimable impurities.
(ii) Crystallisation Principle: Based on the difference in solubilities of the compound and impurities in a suitable solvent.
(iii) Distillation Principle: Liquids having different boiling points vaporise at different temperatures.
* **Used to separate:**
(a) Volatile liquids from non-volatile impurities.
(b) Liquids having sufficient difference in their boiling points.
Types: Fractional distillation and steam distillation
(iv) **Differential Extraction Principle:** Organic compound is shaken with an organic solvent in which it is more soluble than water. Organic solvent and aqueous solution should be immiscible with each other forms two distinct layers which can be separated by separatory funnel.
(v) **Chromatography**
(a)Adsorption Chromatography. Different compounds are adsorbed on an adsorbent to different degrees.
Column Chromatography: Separation of a mixture over a column of adsorbent packed in a glass tube.
Thin Layer Chromatography: Separation of substances of a mixture over a thin layer of an adsorbent coated on a glass tube.
(b)Partition Chromatography Principle: Based on continuous differential partitioning of components of a mixture between stationary and mobile phases.

Important Questions

Multiple Choice questions-

Question 1. Which among the following statement is not true?

(a) In liquid, particles are less regularly arranged and are free to move

(b) Boiling involves breaking up of group of molecules in liquid

(c) Boiling involves separation of oppositely charged ions

(d) Thermal energy of particles overcome cohesive forces that hold them

Question 2. Identify the chiral molecule among the following:

(a) Isopropyl alcohol

(b) 2-pentanol

(c) 1-bromo 3-butene

(d) Isobutyl alcohol

Question 3. Which element is estimated by Carius method?

(a) Carbon

(b) Hydrogen

(c) Halogen

(d) Nitrogen

Question 4. A solution of (+) – 2 – chloro – 2 – phenylethane in toluene racemises slowly in the presence of small amounts of $SbCl_5$ due to the formation of

(a) Carbanion

(b) Carbene

(c) Free radical

(d) Carbocation

Question 5. Which of the following acids has the smallest dissociation constant?

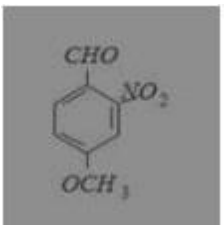
(a) $CH_3CHFCOOH$

(b) FCH_2CH_2COOH

(c) $BrCH_2CH_2COOH$

(d) $CH_3CHBrCOOH$

Question 6. What is the correct IUPAC name of?



(a) 4-methoxy-2-nitrobenzaldehyde

(b) 4-formyl-3-nitro anisole

(c) 4-methoxy-6-nitrobenzaldehyde

(d) 2-formyl-5-methoxy nitrobenzene

Question 7. 0.5 g of hydrocarbon gave 0.9 g water on combustion. The percentage of carbon in hydrocarbon is

(a) 75.8

(b) 80.0

(c) 56.6

(d) 28.6

Question 8. 0.92 g of an organic compound was analysed by combustion method. The mass of the U- tube increased by 1.08 g. What is the percentage of hydrogen in the compound?

(a) 13.04%

(b) 52.17%

(c) 65.21%

(d) 11.30%

Question 9. What is the state of hybridisation of carbon in carbanion?

(a) sp

(b) sp^2

(c) sp^3

(d) sp^2d.

Question 10. An organic compound contains C = 38.8 H = 16 and N = 45.2. Empirical formula of the compound is

(a) CH_3NH_2

(b) CH_3CN

(c) C_2H_5CN

(d) $CH_2(NH)_2$

Question 11. 59 g of an amide obtained from a carboxylic acid, RCOOH, liberated 17 g of ammonia upon heating with alkali. The acid is

(a) Formic Acid

(b) Acetic Acid

(c) Propionic Acid

(d) Benzoic Acid

Question 12. The displacement of electrons in a multiple bond in the presence of attacking reagent is called

(a) Inductive effect

(b) Electrometric effect

(c) Resonance

(d) Hyper conjugation

Question 13. The molecular formula C_5H_{12} contains how many isomeric alkanes?

(a) 1

(b) 2

(c) 3

(d) 4

Question 14. If two compounds have the same empirical formula but different molecular formula, they must have

(a) Different percentage composition

(b) Different molecular weight

(c) Same viscosity

(d) Same vapour density

Question 15. Inductive effect involves

(a) Displacement of σ electrons

(b) Delocalization of π electrons

(c) delocalization of σ-electrons

(d) Displacement of π-electrons

Very Short:

1. What type, of hybridisation, is involved in

(i) planar and

(ii) linear molecules?

2. Arrange the following in increasing order of C – C bond strength:

C_2H_6, $C_2H_4C_2H_2$

3. Arrange the following in decreasing order of C — C bond length:

4. What is the type of hybridisation of C atoms in benzene?

5. What are isomers?

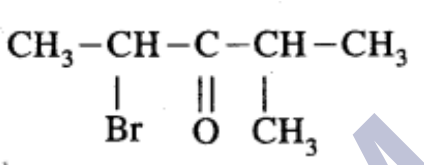
6. Select electrophiles out of the following:

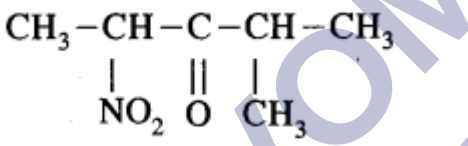
H^+ Na^+, Cl^-, C^2HSOH, $AlCl^3$, SO^3, CN–, CH^3CH^2+,: CCl^2, R-X.

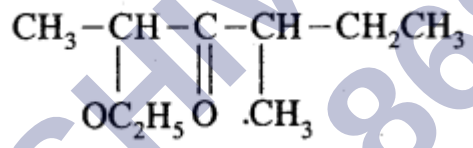
7. Select nucleophiles from the following.

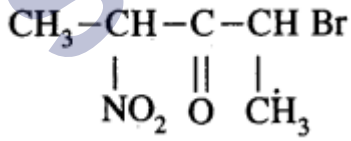
BF_3 NH3 OH–, R-X, C_2H_5OH, H_3O+, NO_2, CN–.

8. Give the I.U.P.A.C. names of the following compounds

(i) 

(ii) 

(iii) 

(iv) 

(v) $(CH_3)4C$

(vi) $(CH_3)_2CHCOOH$.

9. What is a functional group?

10. Arrange the following in increasing order of-I effect.

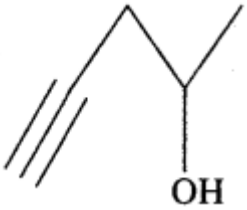
(i) -NO_2, -COOH, -F, -CN, – I.

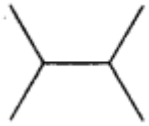
Short Questions:

1. Expand each of the following bond-line formulae to show all the atoms including carbon and hydrogen.

(a) 

(b) 

(c) 

(d) 

2. For each of the following compounds, write a more condensed and also their bond line formulae.

(a) $CH_3-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_2OH$

(b) $CH_3CH_2CH_2CH_2CH_2CH_2\overset{\displaystyle Br}{\overset{|}{C}}H\overset{\displaystyle H}{\overset{|}{C}}H_2C{=}O$

(c) $HO\,CH_2CH_2CH_2CH\,\underset{\displaystyle CH_3}{\underset{|}{CH}}\,\overset{\displaystyle CH_3}{\overset{/}{\backslash}}\,CH_3$

(d) $N{\equiv}C\,\overset{\displaystyle OH}{\overset{|}{C}}H-C{\equiv}N$

3. What is the type of hybridisation of each carbon in the following compounds?

(a) CH_3Cl

(b) $(CH_3)_2CO$

(c) CH_3CN

(d) $HCONH_2$

(e) $CH_3CH = CHCN$.

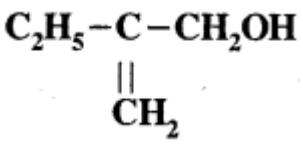
4. What is the shape of the following molecules:

(a) $H_2C = O$

(b) CH_3F

(c) H-C ≡ N?

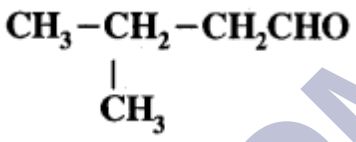
5. Give the I.U.P. A.C. names of the following compounds:

(i) 

(ii) $CH_3 - CH = CH\ COOH$

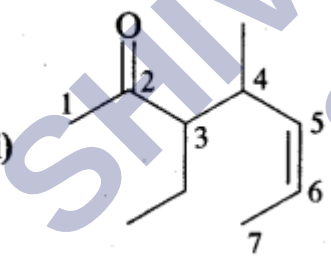
(iii) $(CH_3)_2C = CHCOCH_3$

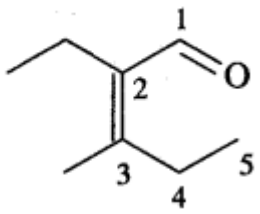
(iv) 

(v) 

(vi) $CH_2 = CH - CN$.

6. Write the I.U.P.A.C. names of

(i) 

(ii) 

Long Questions:

1. Explain the principle of steam distillation.

2. Dehydrobromination of compounds (A) and (B) yield the same alkene (c) Alkene (c) Can regenerate (A) and (B) by the addition of HBr in the presence and absence of peroxide respectively. Hydrolysis of A and B give isomeric products (D) and (E) respectively. 1, 1-Diphenyl ethane is obtained on the reaction of (C) of benzene in the presence of H+ ions. Give structures of A to E with reactions.
3. What are reaction intermediates? How are they generated by bond fission?
4. 0.395 g of an organic compound by various method for the estimation of sulphur gave 0.582g of BaS04. Calculate the percentage of Sulphur.
5. 0.15g of an organic compound gave 0.12g of AgBr by carius method. Find the percentage of bromine in the compound.

Assertion Reason Questions:

1. In the following questions, a statement of Assertion (A) followed by a statement of Reason (R) is given. Choose the correct option out of the choices given below each question.

   Assertion (A) : Simple distillation can help in separating a mixture of propan-1-ol (boiling point 97°C) and propanone (boiling point 56°C).

   Reason (R) : Liquids with a difference of more than 20°C in their boiling points can be separated by simple distillation.

   (i) Both A and R are correct and R is the correct explanation of A.

   (ii) Both A and R are correct but R is not the correct explanation of A.

   (iii) Both A and R are not correct.

   (iv) A is not correct but R is correct.

2. In the following questions, a statement of Assertion (A) followed by a statement of Reason (R) is given. Choose the correct option out of the choices given below each question.

   Assertion (A) : Energy of resonance hybrid is equal to the average of energies of all canonical forms.

   Reason (R) : Resonance hybrid cannot be presented by a single structure.

   (i) Both A and R are correct and R is the correct explanation of A.

   (ii) Both A and R are correct but R is not the correct explanation of A.

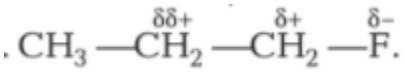
   (iii) Both A and R are not correct.

   (iv) A is not correct but R is correct.

Case Study Based Question:

1. Read the passage given below and answer the following questions:

   The electron displacements due to the influence of an atom or a substituent group present in the molecule cause permanent polarisation of the bond (called electronic effect), e.g.



   In above example, polar C—F bond induce polarity in the adjacent bonds. Such polarisation of adjacent σ- bond is referred to as the inductive effect. This effect decreases rapidly as the number of intervening bonds increases. The resonance effect is defined as the polarity produced in the molecule by the interaction of two π-bonds or in conjugated system.

   When the group or atom release electron density then electron density of conjugated system increases while the group or atom attract/withdraw electron density then electron density of conjugated system decreases.

   (1) In which molecule dipole moment is the maximum?

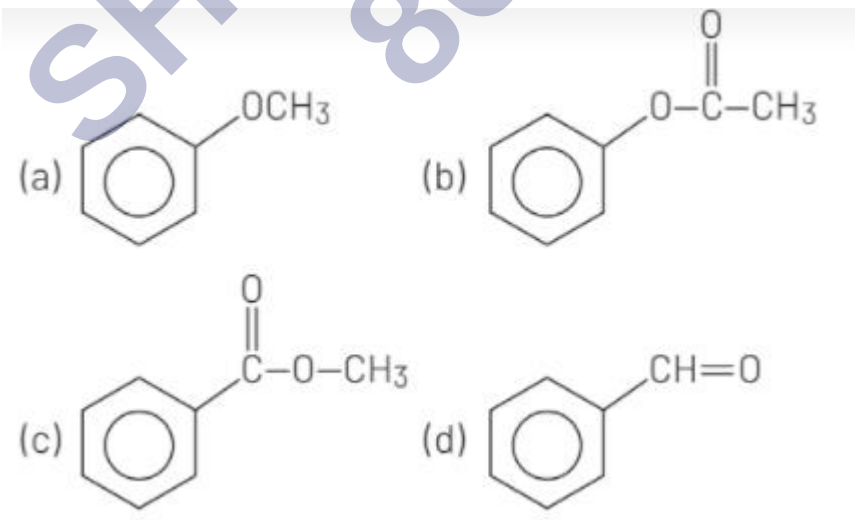
   (a) $CH_3CH_2CH_2—Cl$

   (b) $CH_3CH_2CH_2—NO_2$

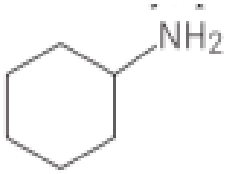
   (c) $CH_3CH_2CH_2—OH$

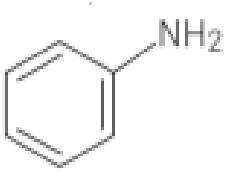
   (d) $CH_3—CH_2—NH—\overset{\overset{O}{\|}}{C}—CH_3$

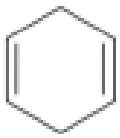
   (2) In which benzene ring electron density is maximum?

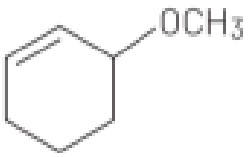


   (3) Which of the following system show abnormal behaviour in their properties (like-stability, polarity ... etc.) ?

(a) 

(b) 

(c) 

(d) 

(4) The permanent displacement of electron through a chain involving only σ-bonds is called

(a) Inductive effect

(b) Hyperconjugation effect

(c) Electrometric effect

(d) Mesmeric effect

2. Read the following passage and answer the question accordingly.

An intermediate is a molecular entity, that is formed from the reactants and reacts further to give the directly observed products of a chemical reaction. Most chemical reactions are stepwise, that is they take more than one elementary step to complete. An intermediate is the reaction product of each of these steps, except for the last one, which forms the final very isolated. Also, owing to the short lifetime, they do not remain in the product mixture.

In certain cases, they are separated and stored. For example matrix isolation and low temperature. Matrix isolation is a technique that is used experimentally in physics and chemistry that includes a material that has been trapped with in an unreactive material. Host matrix generally comprises guest particles that are generally embedded. Guest particles can be molecules, atoms and ions. The guest is isolated within the host matrix.

(1) Relative stabilities of the following carbocations will be in the order

$\overset{\oplus}{C}H_3$, $CH_3\overset{\oplus}{C}H_2$, $\overset{\oplus}{C}H_2OCH_3$
(A) (B) (C)

(a) C > B > A

(b) C < B < A

(c) B > C > A

(d) C > A > B

(2) CH_3 CH_2 Cl undergoes homolytic fission, produces.

(a) $CH_3\dot{C}H_2$ and $\dot{Cl}$ (b) $CH_3\overset{\oplus}{C}H_2$ and Cl^-

(c) $CH_3\overset{\oplus}{C}H_2$ and $\overset{\oplus}{Cl}$ (d) $CH_3\dot{C}H_2$ and Cl^-

(3) The shape of carbocation is:

(a) square planar

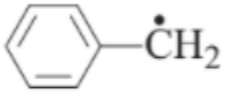
(b) trigonal planar

(c) octahedral

(d) trigonal pyramidal

(4) Compare stability of free radicals.

I. $CH_3—\dot{C}H—CH_3$

II. 

III. $\dot{C}H_2—CH(CH_3)_2$

IV. $\dot{C}H_2—CH_3$

(a) II > I > III > IV

(b) II > I > IV > III

(c) I > II > III > IV

(d) IV > III > I > II

Answer Key:

MCQ

1. (c) Boiling involves separation of oppositely charged ions
2. (d) Isobutyl alcohol
3. (c) Halogen
4. (d) Carbocation
5. (c) $BrCH_2CH_2COOH$
6. (a) 4-methoxy-2-nitrobenzaldehyde

7. (b) 80.0

8. (a) 13.04%

9. (c) sp^3

10. (a) CH_3NH_2

11. (b) Acetic Acid

12. (b) Electrometric effect

13. (c) 3

14. (b) Different molecular weight

15. (a) Displacement of σ electrons

Very Short Answer:

1. (i) sp^2

   (ii) sp.

2. $C_2H_6 < C_2H_4 < C_2H_2$.

3. $C_2H_6 > C_2H_4 > C_2H_2$.

4. It is an sp2 type of hybridisation.

5. Compounds having the same molecular formula, but different physical and chemical properties are called isomers.

6. H^+, Na^+, A1Cl3, SO3, CH3CH_2+,: CCl_2, R-X.

7. NH_3, OH, C_2H_5OH, CN

8. (i) 2-Bromo-4 – methyl pent-3- one

   (ii) 4-Methyl-2-nitro pent – 3 – one

   (iii) 2 – Ethoxy – 4 – methoxypent – 3 – one

   (iv) 2-Bromo-4-nitro pent-3-one

   (v) 2, 2-Dimethylpropane

(vi) 2-Methyl propanoic acid.

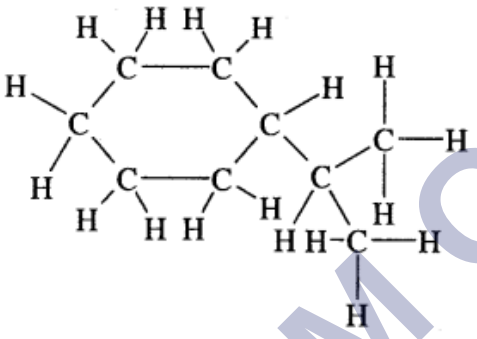
9. The atom or group of atoms present in a molecule that determines its chemical properties is called the functional group.

10. -I < -F < -COOH < -CN <NO_2.

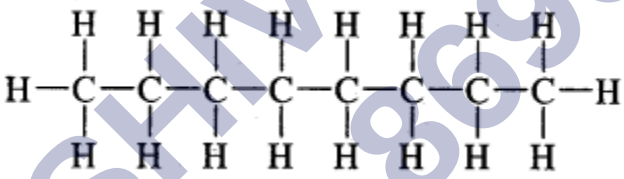
Short Answer:

Ans: 1.

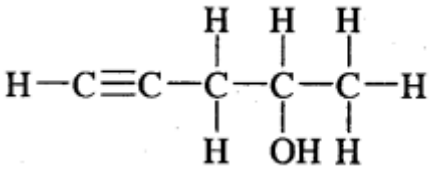
(a)



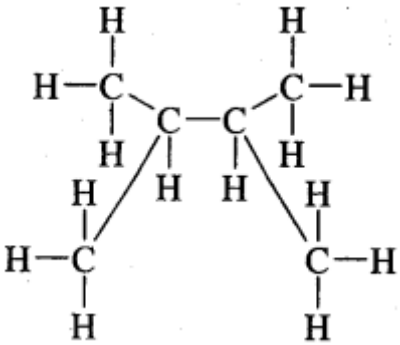
(b)



(c)



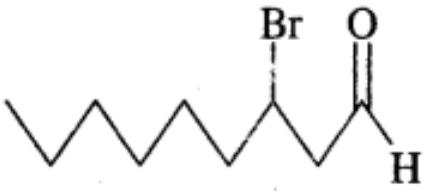
(d)



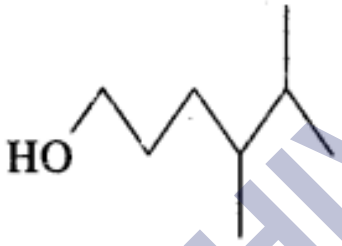
Ans: 2. (a) Condensed formulae are

$(CH_3)2CH\ CH_2\ OH$

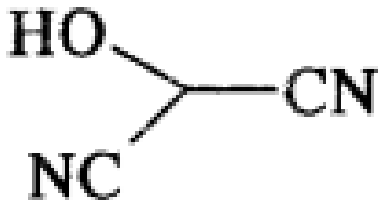
(b) $CH_3(CH_2)_5\ CHBr\ CH_2\ CHO$



(c) $HO(CH_2)_3\ CH(CH_3)\ CH(CH_3)_2$

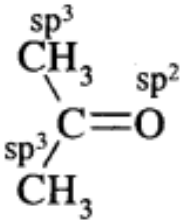


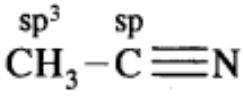
(d) $HOCH(CN)_2$

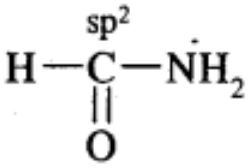


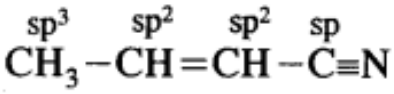
Ans: 3.

(a) $\overset{sp^3}{CH_3}-Cl$

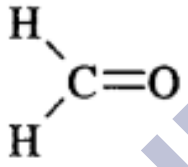
(b) 

(c) 

(d) 

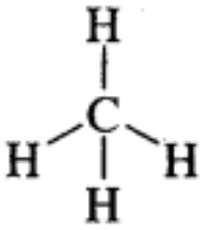
(d) 

Ans: 4. (a) In $H_2C = O$; C is sp^2 hybridised, hence its shape is H trigonal planar



(b) In CH_3F -F; C is sp3 hybridized

∴ it is tetrahedral



(c) In H-C ≡ N; C is sp-hybridized, hence HCN is linear

H—C ≡ N.

Ans: 5. (i) 2-Ethylprop-2-en-l-ol

(ii) But-2-en-l-oic acid

(iii) 4-Methylpent-3-en-2-one

(iv) 3-Chloropropanal

(v) 3-Methylbutane-l-al

(vi) Prop-2-en-1-nitrile.

Ans: 6. (i) 3-Ethyl-4-methylhept-5-en-2-one

(ii) 2-Ethyl-3-methylpent-2-en-1 -one.

Long Answer:

Ans: 1. Steam distillation: The process of steam distillation is employed in the purification of substance from non-volatile impurities provided the substance itself is volatile in steam and insoluble in water.

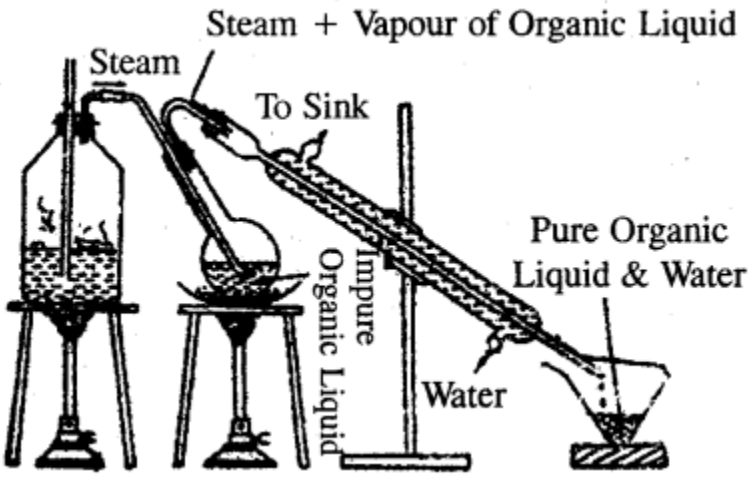
This method is based on the facts that

1. A liquid boils at a temperature when its vapour pressure becomes equal to the atmospheric pressure.

2. The vapour pressure of a mixture of two immiscible liquids is equal to the sum of the vapour pressures of the individual liquids.

In the actual process, steam is continuously passed through the impure organic liquid. Steam heats the liquid and it gets practically condensed to water. After some time, mixture of the liquid and water begins to boil, because the vapour pressure of the mixture becomes equal to the atmospheric pressure.

Obviously, this happens at a temperature that is lower than the boiling point of the substance or that of water. Thus an organic compound boils below its boiling points and chances of decomposition avoided. For example, a mixture of aniline (b.p 453 K) with decomposition and water (b.p. 373 K) under normal atmospheric pressure boils at 371K. At this temperature the



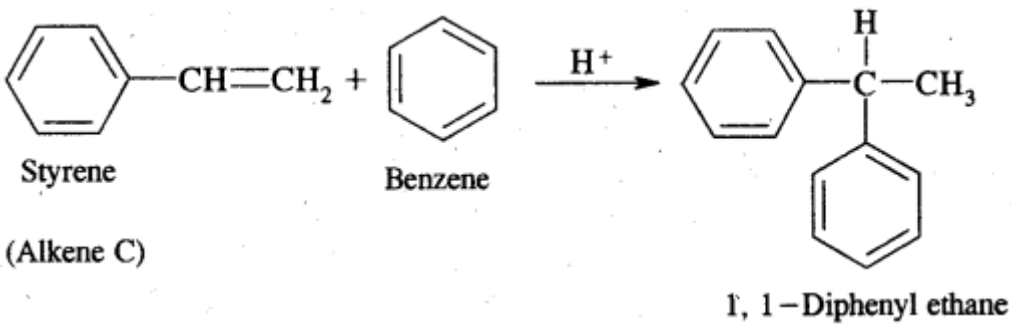
Steam Distillation

water boils at 371 K. At this temperature, the vapour pressure of water is 717 mm and that of aniline is 43 mm and therefore the total pressure is equal, to 760 mm. Thus in steam distillation, the liquid gets distilled at a temperature lower than its boiling point and chances of decomposition avoided. The proportion of water and liquid in the mixture that distils over is given by the relation.

$$\frac{w_1}{w_2} = \frac{P_1 \times 18}{P_2 \times M}$$

where w_1 and w_2 stand for the masses of water and liquid that distils over. P_1 and P_2 are vapour pressure of water and of liquid at the distillation temperature and M is the molecular mass of the liquid.

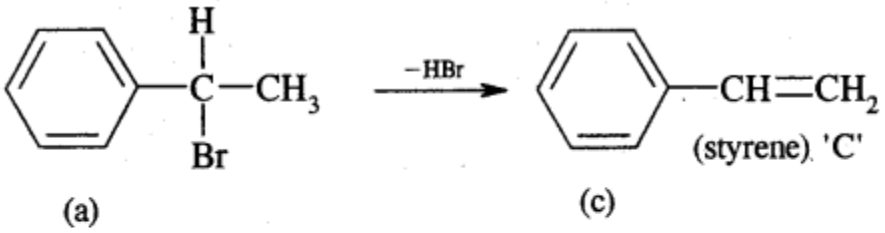
Ans: 2. Alkene (C) on reaction with benzene in the presence of H+ ions give 1, 1-Diphenyl ethane. Therefore, C must be styrene as depicted below



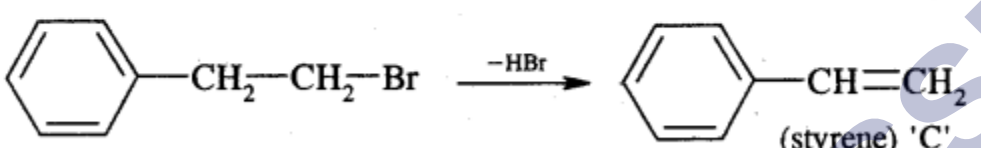
Now dehydrobromination of A and B give the same alkene C, i.e.,

styrene.

∴ A and B must be isomeric alkyl bromide

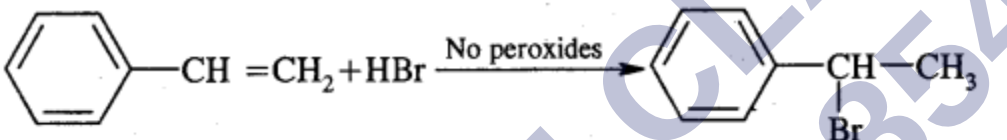


(a) (c)

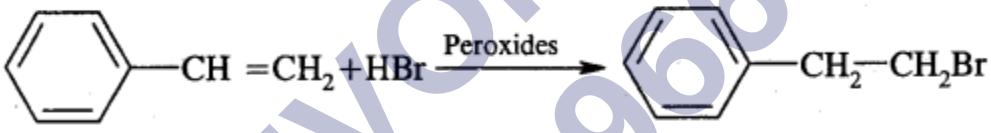


(b) (c)

A and B can be obtained by the addition of HBr in the presence and absence of peroxide to styrene.

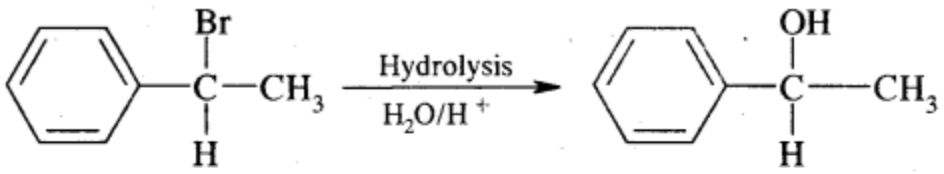


(A)

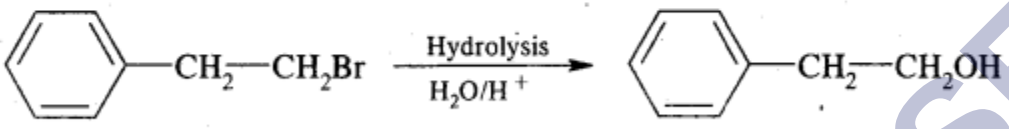


(B)

Hydrolysis of A and B give isomeric alcohols (D) & (E) as



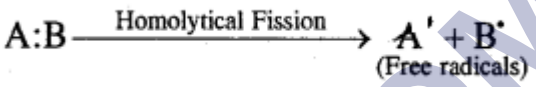
(A) 2-Phenylethan-2-ol (D)



2-Phenylethan-1-ol (E)

Ans: 3. The species which are generated as a result of bond fission are called reaction intermediates. The important reaction intermediates are:

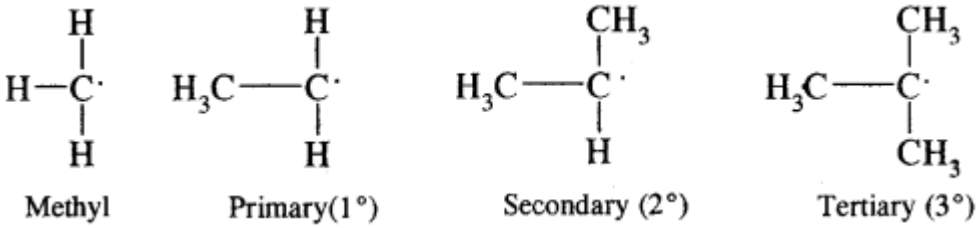
1. Free Radicals: A free radical may be defined as an atom or group of atoms having an impaired electron. These are obtained as a result of homolytic fission of covalent bonds.



These free radicals are neutral particles, extremely transient, (short-lived) and highly reactive. They get consumed as soon as they are formed. They pair up their electron with another electron from wherever it is available. They occur only as a reaction intermediate. Their presence is felt in reactions, but cannot be isolated in a free state. For example dissociation of Cl2 gas in the presence of Ultraviolet light produces free radicals.

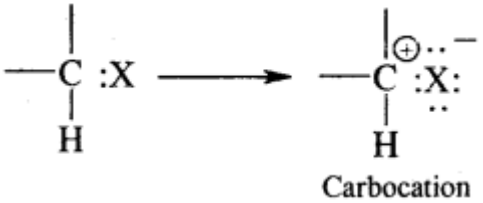
The alkyl free radicals are obtained when free radical: Cl reacts with alkanes.

Free radical may be primary, secondary, tertiary depending upon whether, one, two or three carbon atom attached to the carbon atoms carrying the odd electron.

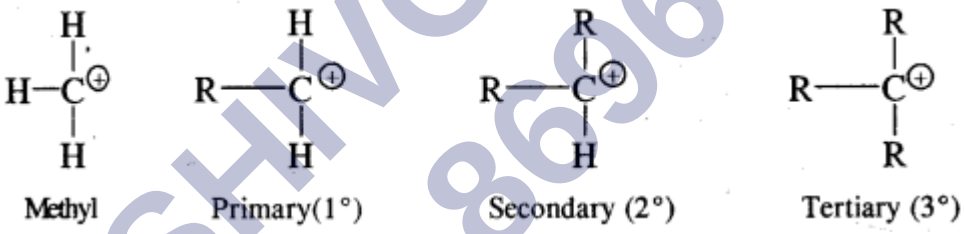


The stability is CH3 < 1° < 2° < 3°.

2. Carbocation or carbonium ion: It is defined as a group of atoms that contain positively charged carbon having only six electrons. It is obtained by heterolytic fission of a covalent bond involving a carbon atom.

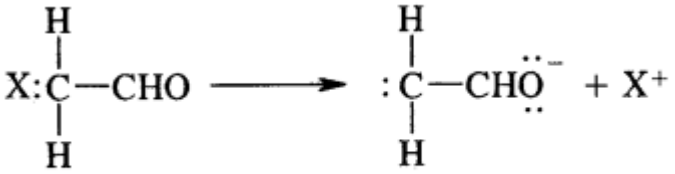


They are also classified as primary, secondary and tertiary depending upon whether one, two or three carbon atoms are attached to the carbon bearing the positive charge as:



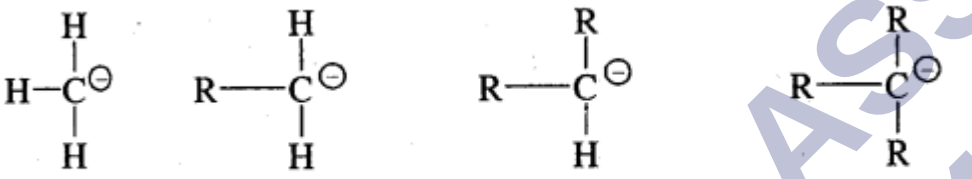
Thus, the order of stability if CH3+ < 1° < 2° < 3°.

3. Carbanion: A carbanion may be defined as a species containing a carbon atom carrying a negative charge. These are generated by the atom in which the atom linked to carbon goes without the bonding electrons. As a result of this carbon acquires a negative charge. For example, the removal of hydrogen of methyl part of acetaldehyde molecule as H+ ion leaving both the electron on carbon.



Carbanion

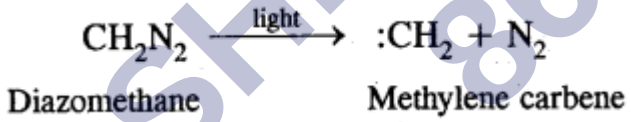
They are also very reactive species. They are also classified as primary, secondary and tertiary depending upon whether one, two or three carbon atoms are attached to the carbon atom bearing negative
charge.



Methyl Primary(1°) Secondary (2°) Tertiary (3°)

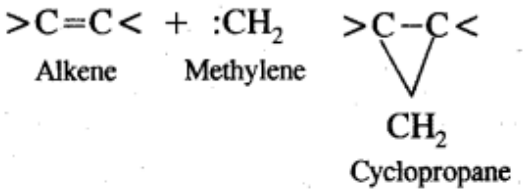
The order of stability is the reverse of free radicals and carbocations
CH_3^- > 1° > 2° > 3°.

(iv) Carbenes: The carbenes are reactive neutral species in which carbon atom has six electrons in the valency shell out of which two are shared. The simplest carbene is methylene (CH2). It is formed when diazomethane is decomposed by the action of light.



Diazomethane Methylene carbene

It is very reactive. It reacts with alkenes by adding to the double bond forming cyclopropane.



Alkene Methylene Cyclopropane

Ans: 4. Mass of $BaSO_4$ = 0.582 g

$BaSO_4$ = S

233 = 32

233g of $BaSO_4$ contain sulphur = 32g

0. 582 g of $BaSO_4$ contains sulphur

$$= \frac{32 \times 0.582}{233}$$

$$\text{Percentage of sulphur} = \frac{\text{Wt. of sulphur}}{\text{Wt. of compound}} \times 100$$

$$= \frac{32 \times 0.582}{233 \times 0.395} \times 100$$

$$= 20.24\%$$

Ans: 5. Mass of AgBr formed = 0.12g

188 g of AgBr contains bromine = 80g.

Therefore, 0.12g of AgBr will contain bromine

$= \frac{80 \times 0.12}{188} = 0.051$ g

Percentage of bromine $= \frac{0.051}{0.15} \times 100 = 34\%$

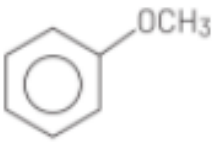
Assertion Reason Answer:

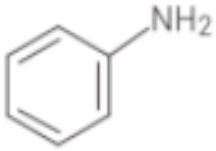
1. (i) Both A and R are correct and R is the correct explanation of A.
2. (iv) A is not correct but R is correct.

Case Study Answer:

1. **Answer:**

(1) (b) $CH_3\ CH_2\ CH_2 — NO_2$

(2) (a) 

(3) (b) 

(4) (a) Inductive effect

2. Answer:

(1) (a) C > B > A

(2) (a) $CH_3\dot{C}H_2$ and $\dot{C}l$

(3) (b) trigonal planar

(4) (b) II > I > IV > III