UNIT-11 FUNDAMENTALS OF ORGANIC CHEMISTRY

MY REVISION TIMELINE:-

SUMMARY:-

- Characteristics of organic chemistry:
  - Covalent compounds, soluble in organic solvent (benzene, toluene, ether, chloroform etc…)
  - Mostly inflammable (except CCl_4), low boiling and melting points.
  - Characterized by functional groups
  - Homologous series: A series of organic compounds each containing a characteristic functional group and the successive members differ from each other in molecular formula.
- Classification of organic compounds:
  - Based on the structure
  - Based on functional groups
- Structural representation of organic compounds:
  - Lewis structure or dot structure
  - Dash structure or line bond structure
  - Condensed structure
  - Bond line structure
- Three dimensional representation of organic molecules:
  - Solid and dashed wedge formula – 3D image of a molecule can be perceived from two dimensional picture.
  - Fisher projection formula – Representing 3D structure in 2D
  - Sawhorse projection formula
  - Newman projection formula
- Isomers – Two or more compounds with same molecular formula but different structure and properties (physical, chemical or both). It is classified into two types:
  - Constitutional isomers
    - Chain
    - Position
    - Functional
    - Metamers
    - Tautomers
    - Ring chain
  - Stereo isomers

- Conformational
- Configurational
  - Geometrical
  - Optical

- Restricted rotation around C=N (oximes) gives rise to geometrical isomerism in oximes. Here 'syn' and 'anti' are used instead of us and trans respectively.
- Detection of elements in organic compounds:
  - Copper (II) oxide Test → To detect carbon and hydrogen
  - Lassaigne sodium fusion test → Test to detect Nitrogen, Sulphur, Halogen and Phosphorous
- Estimation of elements:
  - After detecting the various elements present in a given organic compound by qualitative analysis it is necessary to determine their composition by weight
    - Carius method (For Sulphur, Halogen and Phosphorous)
    - Dumas method and Kjeldahl's method (For nitrogen)
- Purification of organic compounds:
  - Purification of solid by
    - Sublimation
    - Crystallization
    - Fractional crystallization
  - Purification of liquids by
    - Distillation
    - Fractional distillation
    - Steam distillation
    - Distillation under reduced pressure
    - Azeotropic distillation
    - Differential extraction
    - Chromatography
- Chromatography is the most valuable method for the separation and purification of small quantity of mixtures. Types of chromatography
  - Column Chromatography (CC)
  - Thin Layer Chromatography (TLC)
  - Paper Chromatography (PC)
  - Gas-liquid Chromatography
  - Ion-exchange Chromatography

HINTS TO SOLVE PROBLEMS:-

- Percentage of C = $\frac{12}{14} \times \frac{x}{w} \times 100$
  w → weight of the compound
  x → weight of CO_2 compound

- Percentage of H = $\frac{2}{18} \times \frac{x}{w} \times 100$
  x → weight of H_2O compound
- Percentage of S = $\frac{32}{233} \times \frac{x}{w} \times 100$
  x → weight of $BaSO_4$ compound
- Percentage of Cl = $\frac{35.5}{143.5} \times \frac{x}{w} \times 100$
  x → weight of AgCl compound
- Percentage of Br = $\frac{80}{188} \times \frac{x}{w} \times 100$
  x → weight of AgBr compound
- Percentage of I = $\frac{127}{235} \times \frac{x}{w} \times 100$
  x → weight of AgI compound
- Percentage of P = $\frac{31}{1877} \times \frac{x}{w} \times 100$
  x → weight of ammonium molybdate compound
- Percentage of P = $\frac{62}{222} \times \frac{x}{w} \times 100$
  x → weight of $Mg_2P_2O_7$ compound
- Percentage of N by Dumas method = $\frac{28}{22.4} \times \frac{v_o}{w} \times 100$
  v_o → volume of N_2 at STP
- Percentage of N by Kjeldahl's method = $\frac{1.4NV}{W}$
  W → weight of organic compound
  N → Normality of acid
  V → Volume of acid

TEXTBOOK EVALUATION

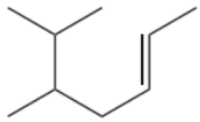
Multiple choice questions:-

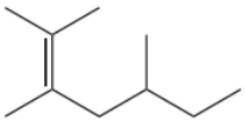
1. Select the molecule which has only one ir bond.
(a) CH_3-CH=CH-CH_3 (b) CH3-CH=CH-CHO
(c) CH3-CH=CH-COOH (d) All of these

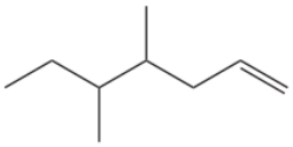
2. In the hydrocarbon $\overset{7}{CH_3}-\overset{6}{CH_2}-\overset{5}{CH}=\overset{4}{CH}-\overset{3}{CH_2}-\overset{2}{C}\equiv\overset{1}{CH}$ the state of hybridisation of carbon 1,2,3,4 and 7 are in the following sequence.
(a) sp, sp, sp^3, sp^2, sp^3 (b) sp, sp, sp^3, sp^2, sp^3
(c) sp, sp, sp^2, sp, sp^3 (d) none of these

3. The general formula for alkadiene is
(a) C_nH_{2n} (b) C_nH_{2n-1}
(c) C_nH_{2n-2} (d) C_nH_{n-2}

4. Structure of the compound whose IUPAC name is 5, 6 – dimethylhept-2-ene is

a) 

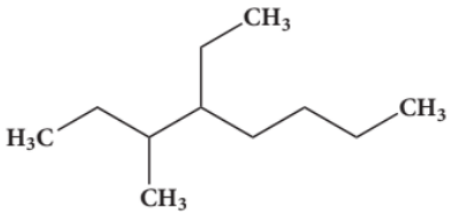
b) 

c) 

d) None of these

Ans: Option a

5. The IUPAC name of the compound is



(a) 2,3 – Diemethyiheptane (b) 3 – Methyl – 4 – ethyloctane

(c) 5 – ethyl – 6 – methyloctane **(d) 4 – Ethyl -3 – methyloctane.**

6. Which one of the following names does not fit a real name?

(a) 3 – Methyl – 3 – hexanone (b) 4- Methyl – 3 – hexanone

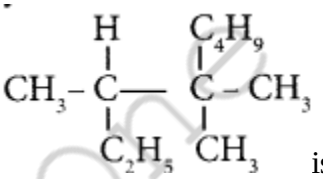
(c) 3 – Methyl – 3 – hexanol (d) 2 – Methyl cyclo hexanone.

7. The IUPAC name of the compound CH3-CH = CH-C≡CH is

(a) Pent – 4 – yn – 2 – ene **(b) Pent -3-en – 1- yne**

(c) pent – 2 – en – 4 – yne (d) Pent – 1 – yn – 3 – ene

8. IUPAC name of

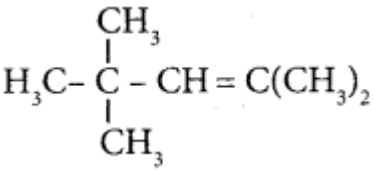


is

(a) 3, 4, 4 – Trimethylheptane (b) 2 – Ethyl – 3, 3 – dimethyl heptane

(c) 3, 4, 4 – Trimethyloctane (d) 2 Butyl – 2 -methyl – 3 – ethyl-butane.

9. The IUPAC name of

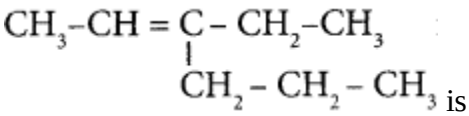


is

(a) 2, 4. 4 – Trimethylpent -2-ene **(b) 2, 4. 4 – Trimethylpent -3-ene**

(c) 2, 2, 4 – Trimethylpent -3-ene (d) 2, 2, 4 – Trimethylpent -2-ene

10. The IUPAC name of the compound

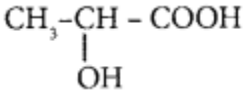


is

(a) 3 – Ethyl – 2- hexene (b) 3 – Propyl – 3. hexene

(c) 4 – Ethyl – 4 – hexene (d) 3 – Propyl -2-hexene

11. The IUPAC name of the compound

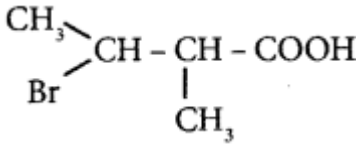


is

(a) 2 – Hydroxypropionic acid **(b) 2 – Hydroxy Propanoic acid**

(c) Propan 2 – ol – 1 – oic acid (d) 1 – Carboxyethanol

12. The IUPAC name of



is

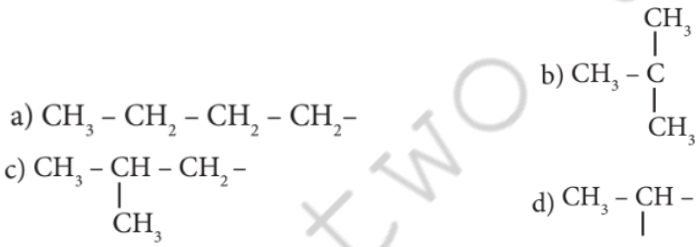
(a) 2 – Bromo – 3 – methylbutanoic acid

(b) 2 – methyl – 3 – bromobutanoic acid

(c) 3 – Bromo – 2 – methylbutanoic acid

(d) 3 – Bromo – 2. 3 – dimethyl propanoic acid

13. The structure of isobutyl group in an organic compound is



Ans: Option c

14. The number of stereoisomers of 1, 2-dihydroxycyclopentane is

(a) 1 (b) 2

(c) 3 (d) 4

15. Which of the following is optically active?

(a) 3 – Chioropentane (b) 2 – Chioropropane

(c) Meso – tat-tat-ic acid **(d) Glucose**

16. The isomer of ethanol is

(a) acetaldehyde **(b) dimethylether**

(c) acetone (d) methyl carbinol

17. How many cyclic and acyclic isomers are possible for the molecular formula C_3H_6O?

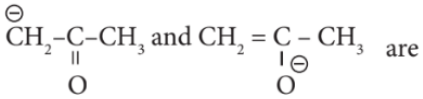
(a) 4 (b) 5

(c) 9 (d) 10

18. Which one of the following shows functional isomerism?

(a) ethylene (b) Propane

(c) ethanol (d) CH_2Cl_2

19.  are

(a) resonating structure **(b) tautomers**

(c) optical isomers (d) conformers

20. Nitrogen detection in an organic compound is earned out by Lassaigne's test. The blue colour formed is due to the formation of

(a) $Fe_3[Fe(CN)_6]_2$ **(b) $Fe_4[Fe(CN)_6]_3$**

(c) $Fe_4[Fe(CN)_6]_2$ (d) $Fe_3[Fe(CN)_6]_3$

21. Lassaigne's test for the detection of nitrogen fails in

(a) H_2N -CO – NH. NH_2. HCl (b) $NH_2 – NH_2$. HCl

(c) $C_6H_5 – NH – NH_2$. HCl (d) $C_6H_5CONH_2$

22. Connect pair of compounds which give blue colouration/precipitate and white precipitate respectively, when their Lassaigne's test is separately done.

(a) NH_2NH_2HCl and $ClCH_2 – CHO$ (b) $NH_2CS\ NH_2$ and $CH_3 – CH2Cl$

(c) $NH_2CH_2\ COOH$ and NH_2CONH_2 **(d) $C_6H_5NH_2$ and $ClCH_2 – CHO$**

23. Sodium nitropruside reacts with suiphide ion to give a purple colour due to the formation of

(a) $[Fe(CN)_5N0]^{3-}$ (b) $[Fe(NO)_5CN]^{+}$

(c) $[Fe(CN)_5NOS]^{4-}$ (d) $[Fe(CN)_5NOS]^{3-}$

24. An organic compound weighing 0.15 g gave on carius estimation, 0.12 g of silver bromide. The percentage of bromine in the compound will be close to

(a) 46% **(b) 34%**

(c) 3.4% (d) 4.6%

25. A sample of 0.5g of an organic compound was treated according to Kjeldahl's method. The ammonia evolved was absorbed in 50 mL of 0.5M H_2SO_4. The remaining acid after neutralisation by ammonia consumed 80 mL of 0.5 M NaOH, The percentage of nitrogen in the organic compound is

(a) 14% **(b) 28%**

(c) 42% (d) 56%

26. In an organic compound, phosphorus is estimated as

(a) $Mg_2P_2O_7$ (b) $Mg_3(PO_4)_2$

(c) H_3PO_4 (d) P_2O_5

27. Ortho and para-nitro phenol can be separated by

(a) azeotropic distillation (b) destructive distillation

(c) steam distillation (d) cannot be separated

28. The purity of an organic compound is determined by

(a) Chromatography (b) Crystallisation

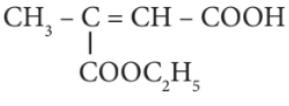
(c) melting or boiling point **(d) both (a) and (c)**

29. A liquid which decomposes at its boiling point can be purified by

(a) distillation at atmospheric pressure **(b) distillation under reduced pressure**

(c) fractional distillation (d) steam distillation

30. Assertion:



is 3-carbethoxy -2- butenoicacid.

Reason: The principal functional group gets lowest number followed by double bond (or) triple bond.

(a) both the assertion and reason are true and the reason is the correct explanation of assertion.

(b) both assertion and reason are true and the reason is not the correct explanation of assertion.

(c) assertion is true but reason is false

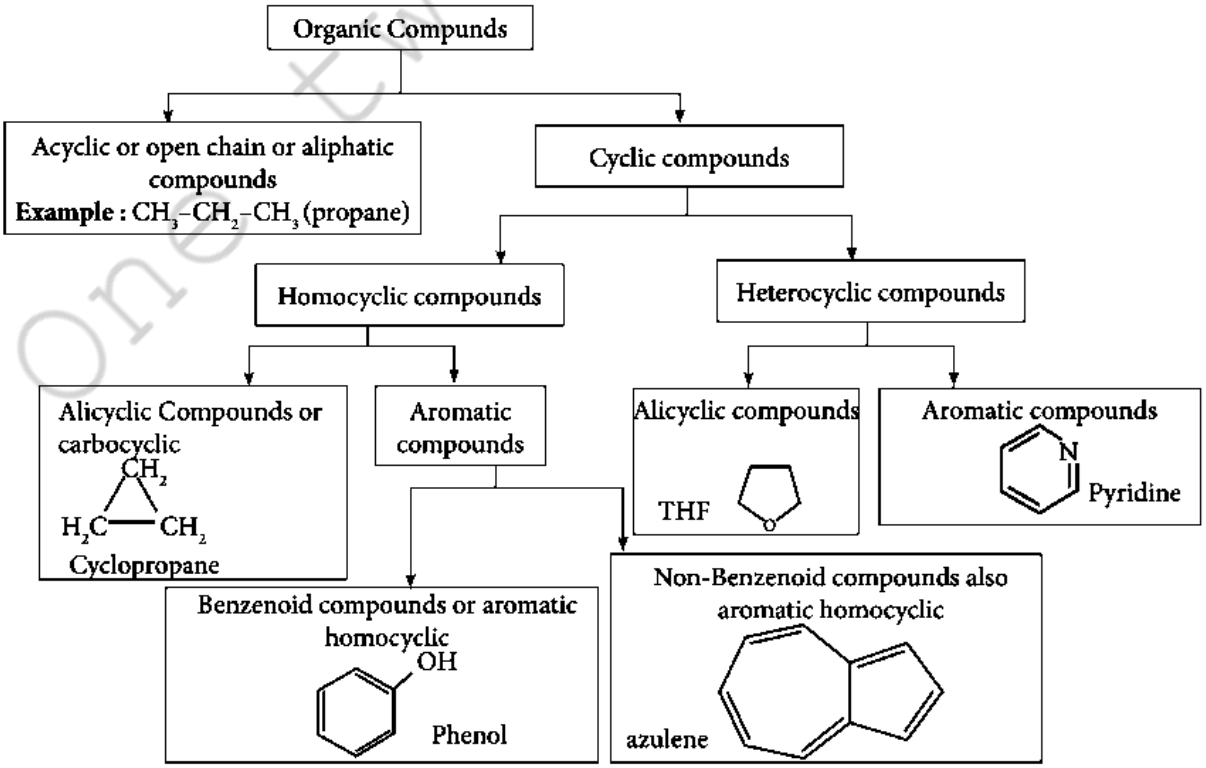
(d both the assertion and reason are false.

Write brief answers to the following questions:-

31. Give the general characteristics of organic compounds?

- All organic compounds are covalent compounds of carbon and are **insoluble** in **water** and **soluble** in **organic solvents**.
- They are **inflammable** (except CCl_4)
- They possess **low boiling** and **melting points** due to their covalent nature.
- They are characterised by **functional groups**.
- They exhibit **isomerism**.

32. Describe the classification of organic compounds based on their structure.



33. Write a note on homologous series.

- A series of organic compounds each containing a **characteristic functional group** and the successive members differ from each other in molecular formula by a **CH_2 group** is called homologous series.
- Example: Methane (CH_4), Ethane (C_2H_6), Propane (C_3H_8) etc…
- Compounds of homologous series are represented by a general formula:
  - Alkane $\mathbf{C_nH_{2n+2}}$
  - Alkene $\mathbf{C_nH_{2n}}$
  - Alkynes $\mathbf{C_nH_{2n-2}}$

34. What is meant by a functional group? Identify the functional group in the following compounds.
(a) acetaldehyde (b) oxalic acid
(c) di methyl ether (d) methylamine

- A functional group is an atom or a specific combination of bonded atoms that react in a characteristic way irrespective of the organic molecule in which it is present.
  - Acetaldehyde = **-CHO**
  - Oxalic acid = **-COOH**
  - Di methyl ether = **-O-**
  - Methyamine = **$-NH_2$**

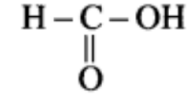
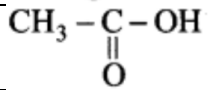
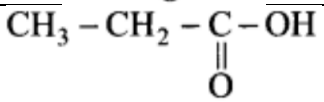
35. Give the general formula for the following classes of organic compounds
(a) Aliphatic monohydric alcohol
(b) Aliphatic ketones.
(c) Aliphatic amines.

- Aliphatic monohydric alcohol = R-OH
- Aliphatic ketones = R-C(=O)-R´
- Aliphatic amines = $R\text{-}NH_2$

36. Write the molecular formula of the first six members of homologous series of nitro alkanes.

- CH_2NO_2 = Nitromethane
- $CH_2\text{-}CH_2NO_2$ = Nitroethane
- $CH_3\text{-}CH_2\text{-}CH_2NO_2$ = 1- nitropropane
- $CH_3\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}NO_2$ = 1- nitrobutane
- $CH_3\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}NO_2$ = 1 – nitropentane
- $CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}NO_2$ = 1- nitrohexane

37. Write the molecular and possible structural formula of the first four members of homologous series of carboxylic acids.

Name	Molecular formula	Structural formula
Formic acid	HCOOH	
Acetic acid	CH_3COOH	
Propionic acid	$CH_3\text{-}CH\text{-}COOH$	

Butyric acid	CH_3-CH_2-CH_2-COOH	$CH_3-CH_2-CH_2-\underset{\underset{O}{\|}}{C}-OH$

38. Give the IUPAC names of the following compounds.

(i) $(CH_3)_2CH–CH_2–CH(CH_3)–CH(CH_3)_2$

(ii) CH_3-$\underset{\underset{CH_3}{|}}{CH}$-$\underset{\underset{Br}{|}}{CH}$-$CH_3$

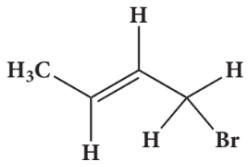
(iii) CH_3-O-CH_3

(iv) CH_3-CH_2-$\underset{\underset{OH}{|}}{CH}$-CHO

(v) $CH_2 = CH-CH=CH_2$

(vi) CH_3-C≡C-$\underset{\underset{Cl}{|}}{CH}$-$CH_3$

(vii)



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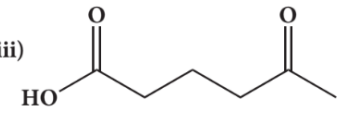

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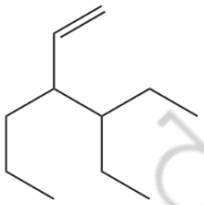

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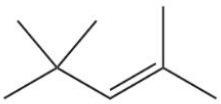

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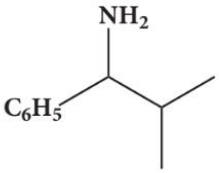

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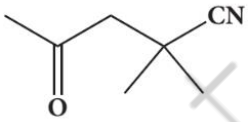

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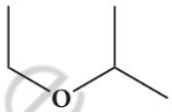

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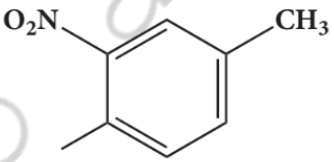
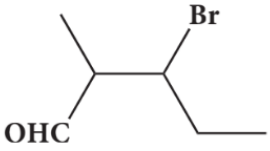


(xv)

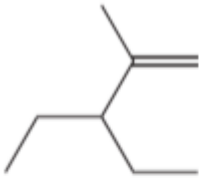


(i) 2,3,5-trimethylhexane
(ii) 2-bromo-3-methylbutane
(iii) methoxymethane
(iv) 2-hydroxybutanal
(v) buta-1,3-diene
(vi) 4-chloropent-2-yne
(vii) 1 -bromobut-2-ene
(viii) 5-oxohexanoic acid
(ix) 3-ethyl-4-ethenylheptane
(x) 2, 4, 4-trimethylpent-2-ene
(xi) 2- methyl-I -phenylpropan- 1 -amine
(xii) 2,2- dimethyl-4-oxopentanenitrile
(xiii) 2-ethoxypropane

(xiv) I -fluoro-4-methyl-2-nitrobenzene
(xv) 3-bromo-2-methylpentanal

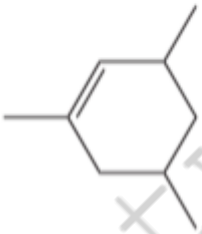
39. Give the structure for the following compound.
(i) 3 – ethyl – 2 methyl -1 – pentene
(ii) 1, 3, 5 – Tnmethyl cyclohex – 1 – ene
(iii) tertiary butyl iodide
(iv) 3 – Chlorobutanal
(y) 3 – Chlorobutanol .
(vi) 2 – Chloro – 2 – methyl propane
(vii) 2, 2-dimethyl- 1 – chioropropane
(viii) 3 – methylbut – 1 – ene
(ix) Butan – 2, 2 – diol
(x) Octane – 1 ,3 – diene
(xi) 1 ,5 – Dimethylcyclohexane
(xii) 2 – Chlorobut – 3 – ene
(xiii) 2 – methylbutan – 3 – ol
(xiv) acetaldehyde

(i)



3-ethyl-2-methyl-1-pentene

(ii)

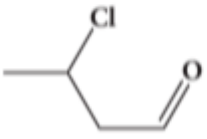


1,3,5-trimethylcyclohex-1-ene

(iii)

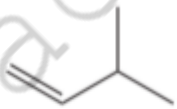
tertiarybutyl iodide

(iv)



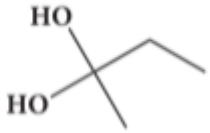
3-Chlorobutanal

(viii)



3-methylbut-1-ene

(ix)

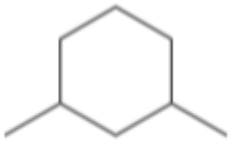


butan-2,2-diol

(x)

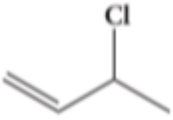
octan-1,3-diene

(xi)



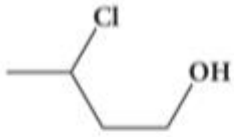
1,3-dimethylcyclohexane

(xii)



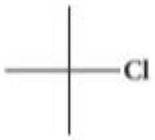
3-chlorobut-1-ene

(v)



3-Chlorobutanol

(vi)

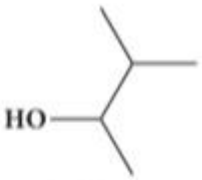


2-chloro-2-methylpropane

(vii)

2.2-dimethyl-1-chloropropane

(xiii)



3-methylbutan-2-ol

(xiv)

acetaldehyde

40. Describe the reactions involved in the detection of nitrogen in an organic compound by Lassaigne method.

- A **small piece of Na** dried by pressing between the folds of a filter paper is taken in a **fusion tube** and it is gently heated.
- When it melts to a **shining globule**, put a pinch of the organic compound on it.
- Heat the tube till the reaction ceases and becomes **red hot**.
- Plunge it in about **50ml** of distilled water taken in a china dish and break the bottom of the tube by striking against the dish.
- Boil the contents of the dish for about 10 minutes and filter. This filtrate is known as **lassaignes extract** or **sodium fusion extract** and it is used for detection of nitrogen, sulphur and halogens present in organic compounds.
- If nitrogen is present it gets converted into **sodium cyanide**.

$$Na + \underbrace{C + N}_{\text{from organic compounds}} \longrightarrow NaCN$$

- Sodium cyanide reacts with freshly prepared ferrous sulphate or ferric ion followed by conc. HCl and gives a **Prussian blue color** or **green color precipitate**. It confirms the presence of nitrogen.
- HCl is added to dissolve the greenish precipitate of ferrous hydroxide produced by the excess of NaOH on $FeSO_4$ which could otherwise mark the Prussian blue precipitate.

$$\underset{\text{(from excess of sodium)}}{FeSO_4 + 2NaOH} \longrightarrow Fe(OH)_2 + Na_2SO_4$$

$$6NaCN + Fe(OH)_2 \longrightarrow \underset{\text{sod.ferrocyanide}}{Na_4[Fe(CN)_6]} + 2NaOH$$

$$3Na_4[Fe(CN)_6] + 4FeCl_3 \longrightarrow \underset{\substack{\text{ferric ferrocyanide} \\ \text{Prussian blue or green ppt}}}{Fe_4[Fe(CN)_6]_3} + 12\,NaCl$$

41. Give the principle involved in the estimation of halogen in an organic compound by carius method.

- A known mass of the organic compound is heated with **fuming HNO_3** and **$AgNO_3$**.
- C, H and S gets oxidised to CO_2, H_2O and SO_2 and halogen combines with **$AgNO_3$** to form a **precipitate** of **silver halide**.

$$X \xrightarrow[AgNO_3]{fum.HNO_3} AgX\downarrow.$$

- The precipitate AgX is **filtered**, **washed**, **dried** and **weighed**.
- From the mass of AgX and the mass of organic compound taken, the **percentage of halogens** are calculated.
- A known mass of the substance is taken along with **fuming HNO_3** and **$AgNO_3$** is taken in a **clean carius tube**.
- The open end of the Carius tube is sealed and placed in an iron tube for **5 hours** in the range at **530-540 K**.
- Then the **tube** is allowed to **cool** and a **small hole** is made in the tube to allow gases produced to escape.
- The tube is broken and the ppt is filtered, washed, dried and weighed. From the mass of AgX obtained, percentage of halogen in the organic compound is calculated.

Weight of the organic compound = w g

Let weight of AgCl precipitate = 'a' g
143.5 g of AgCl contains 35.5 g of Cl
∴ a g of AgCl contains $\frac{35.5}{143.5} \times a$
w g of organic compound gives a g AgCl
Percentage of Cl in w g = $(\frac{35.5}{143.5} \times \frac{a}{w} \times 100)$% organic compound.

Let weight of silver bromide precipitate = 'b' g
188 g of AgBr contains 80 g of Br
∴ b g of AgBr contains $\frac{80}{188} \times b$
w g of organic compound gives b g AgBr
Percentage of Br in w g = $(\frac{80}{188} \times \frac{b}{w} \times 100)$% organic compound.

Let weight of AgI precipitate = 'c' g
235 g of AgI contains 127 g of I
∴ a g of AgI contains $\frac{127}{235} \times c$
w g of organic compound gives a g AgI
Percentage of I in w g = $(\frac{127}{235} \times \frac{c}{w} \times 100)$% organic compound.

42. Give a brief description of the principles of
i) Fractional distillation
ii) Column Chromatography

- **Fractional distillation:**
  - This is one method to **purify** and **separate liquids** present in the mixture having their boiling point close to each other.

- In the fractional distillation, a fractionating column is fitted with **distillation flask** and a **condenser**.
- A **thermometer** is fitted in the fractionating column near the mouth of the condenser. This will enable to record the **temperature of vapour** passing over the condenser.
- The process of separation of the components in a **liquid mixture** at their **respective boiling points** in the form of vapours and the subsequent condensation of those vapours is called **fractional distillation**.
- The process of fractional distillation is repeated, if necessary. This method finds a remarkable application in **distillation of petroleum**, **coal-tar** and **crude oil**.

➢ **Column Chromatography:**

- This is the simplest chromatographic method carried out in long glass column having a **stop cock** near the lower end.
- This method involves separation of a mixture over a column of **adsorbent** (Stationery phase) packed in a column.
- In the column a plug of **cotton** or **glass wool** is placed at the lower end of the column to support the adsorbent powder.
- The tube is uniformly packed with suitable absorbent constitute the stationary phase **(Activated aluminum oxides (alumina), Magnesium oxide, starch are also used as absorbents).**
- The mixture to be separated is placed on the top of the adsorbent column. **Eluent** which is a liquid or a mixture of liquids is allowed to flow down the column slowly.
- Different components are eluted depending upon the degree to which the components are adsorbed and complete separation takes place.
- The most readily **adsorbed substances** are **retained near the top** and others come down to various distances in the column.

43. Explain paper chromatography.

➢ Paper chromatography is an example of **partition chromatography**. A **strip** of **paper** acts as an **adsorbent**. This method involves continues differential partitioning of components of a mixture between **stationary** and **mobile phase**. In paper chromatography, a special quality paper known as **chromatographic paper** is used. This paper act as a **stationary phase**.

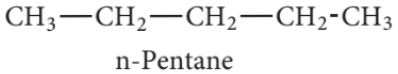
➢ A strip of chromatographic paper spotted at the base with the solution of the mixture is suspended in a **suitable solvent** which acts as the **mobile phase**. The solvent rises up and flows over the spot. The paper selectivity retains different components according to their different partition in the **two phases** where a **chromatogram** is developed.

➢ The spots of the **separated coloured components** are visible at different heights from the position of initial spots on the chromatogram. The spots of the separated colourless compounds may be observed either under **ultraviolet light** or by the use of an **appropriate spray reagent**.

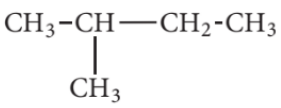
44. Explain various types of constitutional isomerism (structural isomerism) in organic compounds.

Constitutional isomers are isomers having the **same molecular formula but differ in their bonding sequence**. It is classified into **six** types:

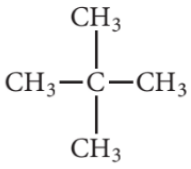
- **Chain (or) nuclear (or) skeletal isomerism**: The phenomenon in which the isomers have **similar molecular formula** but **differ** in the **nature of carbon skeleton** (i.e., straight (or) branched). **Example: C_5H_{12}**



n-Pentane

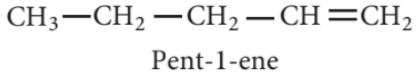


Isopentane
2-methyl butane



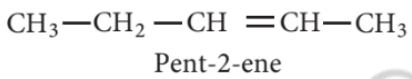
Neopentane
2,2-dimethyl propane

- **Position isomerism:** If different **compounds** belonging to **same homologous series** with the same molecular formula and carbon skeleton but **differ** in the position of **substituent or functional group** or an **unsaturated linkage** are said to exhibit position isomerism. **Example: C_5H_{10}**



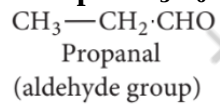
Pent-1-ene

and

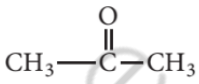


Pent-2-ene

- **Functional isomerism:** Different compounds having **same molecular formula** but **different functional groups** are said to exhibit functional isomerism.
Example: C_3H_6O

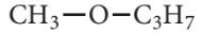


Propanal
(aldehyde group)

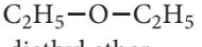


Propanone
(keto group)

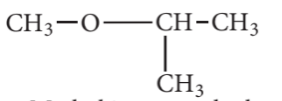
- **Metamerism:** This isomerism arises due to the **unequal distribution of carbon atoms** on either side of the functional group or different alkyl groups attached to either side of the same functional group and having same molecular formula.
Example: $C_4H_{10}O$



Methyl propyl ether
1-methoxypropane



diethyl ether
ethoxyethane



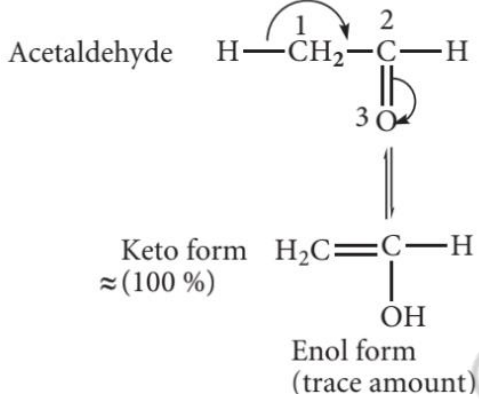
Methyl iso-propyl ether
2-methoxypropane

- **Tautomerism:** It is an isomerism in which a **single compound** exists in **two readily inter convertible structures** that differ markedly in the relative position of atleast one atomic nucleus **generally hydrogen**. There are several types of tautomerism and the two important types are dyad and triad.
  - **Dyad system:** In this system hydrogen atom oscillates between **two directly linked polyvalent atoms**. **Example:**

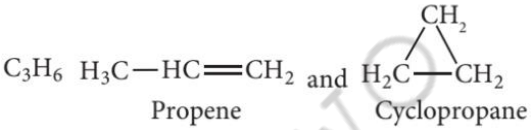
    $H-C\equiv N \longleftrightarrow H-N\equiv C$

    (hydrogencyanide) (hydrogen isocyanide)

    In this example hydrogen atom oscillated between **carbon** and **nitrogen** atoms.
  - **Dyad system:** In this system hydrogen atom oscillates between **three directly linked polyvalent atoms**. **Example:**



- **Ring chain isomerism:** It is an isomerism in which compounds having same molecular formula but **differ** in terms of **bonding of carbon atom** to form **open chain** and **cyclic** structures. **Example: C_3H_6**



45. Describe optical isomerism with suitable example.

- Compounds having **same physical** and **chemical property** but differ only in the **rotation of plane of polarised light** are known as **optical isomers** and the phenomenon is known as **optical isomerism**.
- **Glucose** have the ability to rotate the plane of plane polarised light and it is said to be an **optically active compound** and this property of any compound is called **optical activity**.
- The optical isomer which rotates the plane of plane polarised light to the **right** or in **clockwise direction** is said to be **dextrorotatory** and is denoted by the sign **(+)** or **'d'**.
- The optical isomer which rotates the plane of plane polarised light to the **left** or in **anti- clockwise direction** is said to be **lavorotatory** and is denoted by the sign **(-)** or **'l'**.

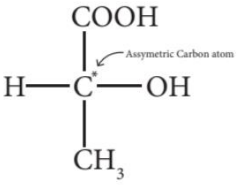
Enantiomerism and optical activity:

An optically active substance may exist in two or more isomeric forms which have **same physical** and **chemical properties** but differ in terms of **direction** of **rotation of plane polarised light** with **equal angle** but in **opposite direction** are known as **enantiomers** and the phenomenon is known as **enantiomerism**.

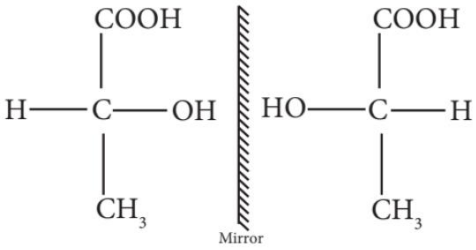
Isomers which are **non-super impossible mirror images** of each other are called **enantiomers**.

Conditions for enantiomerism or optical isomerism:

- A carbon atom whose **tetra valency** is satisfied by four different substituents is called **asymmetric carbon** or **chiral carbon**. It is indicated by an asterisk as **C***.
- A molecule possessing **chiral carbon atom** and **non-super impossible** to its own mirror image is said to be chiral molecule or asymmetric and the property is called **chirality** or **dissymmetry**.

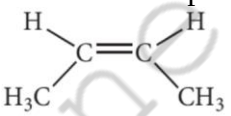


(Lactic Acid)

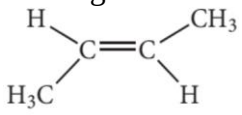


46. Briefly explain geometrical isomerism in alkene by considering 2- butene as an example.

- Geometrical isomers are the **stereoisomers** which have different arrangement of groups or atoms around a rigid frame work of **double bonds**. This type of isomerism occurs due to **restricted rotation of double bonds**, or about **single bonds** in **cyclic compounds**.
- In alkenes, the **carbon-carbon double bond** is **sp^2 hybridized**. The carbon-carbon double bond consists of a **σ bond** and a **π bond**. The σ bond is formed by the **head** on **overlap** of **sp^2** hybrid orbitals. The π bond is formed by the **side wise overlap** of **'p'** orbitals.
- The presence of the π bond **lock** the **molecule** in **one position**. Hence, rotation around **C=C** bond is not possible. This restriction of rotation about C-C double bond is responsible for geometrical isomerism in alkenes.



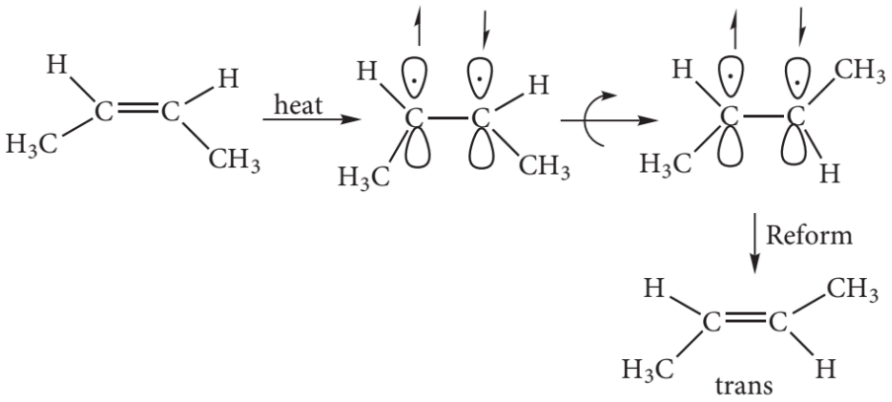
cis - 2-butene



Trans 2-butene

- These two compounds are termed as geometrical isomers and are distinguished from each other by the terms **cis** and **trans**.
- The cis isomer is one in which **two similar groups** are on the **same side** of the double bond.
- The trans isomers is that in which the **two similar groups** are on the **opposite side** of the double bond, hence this type of isomerism is often called **cis-trans isomerism.**
- The cis-isomer can be converted to trans isomer or vice versa is only if either isomer is **heated** to a **high temperature** or **absorbs light**. The heat supplies the energy (about 62kcal/ mole) to break the **π bond** so that rotation about **σ bond** becomes possible. Upon cooling, the reformation of the π bond can take place in

two ways giving a mixture both cis and trans forms of **trans-2-butene** and **cis-2-butene.**



- Generally the **trans isomer** is **more stable** than the corresponding **cis isomers**. This is because in the **cis isomer**, the **bulky groups** are on the **same side** of the double bond.
- The **steric repulsion** of the groups makes the **cis isomers less stable** than the trans isomers in which bulky groups are on the opposite side.
- These cis and trans isomers have **different chemical properties**.
- They can be separated by **fractional distillation, gas chromatography** etc…
- All alkenes with **identical substrate** do not show geometrical isomerism.
- Geometrical isomerism is possible only when each double bonded C atom is attached to **two different atoms or groups** eg. In **propene** no geometrical isomers are possible because one of the double bonded carbon has two identical H atoms.

47. 0.30 g of a substance gives 0.88 g of carbon dioxide and 0.54 g of water. Calculate the percentage of carbon and hydrogen in it.

Given:

Weight of the organic compound = 0.3g

Weight of carbon dioxide = 0.88g

Weight of water = 0.54g

Formula used:

Percentage of C = $\frac{12}{14} \times \frac{x}{w} \times 100$

Percentage of H = $\frac{2}{18} \times \frac{x}{w} \times 100$

Solution:

Percentage of C = $\frac{12}{14} \times \frac{x}{w} \times 100$

Percentage of C = $\frac{12}{14} \times \frac{0.88}{0.3} \times 100$

Percentage of C = 80%

Percentage of H = $\frac{2}{18} \times \frac{x}{w} \times 100$

Percentage of H = $\frac{2}{18} \times \frac{0.54}{0.3} \times 100$

Percentage of H = 20%

48. The ammonia evolved form 0.20 g of an organic compound by kjeldahl method neutralised 15ml of N/20 sulphare acid solution. Calculate the percentage of Nitrogen.

Given:
Weight of organic compound = 0.20g
Normality N = 1/20
Volume V = 15ml
Formula used:
Percentage of nitrogen = $\frac{1.4NV}{W}$
Solution:
Percentage of nitrogen = $\frac{1.4NV}{W}$
Percentage of nitrogen = $\frac{1.4\times\frac{1}{20}\times 15}{0.2}$

Percentage of nitrogen = 5.25%

49. 0.32 g of an organic compound, after heating with fuming nitric acid and barium nitrate crystals is a sealed tube game 0.466 g of barium sulphate. Determine the percentage of sulphur in the compound.
Given:
Weight of organic compound = 0.32g
Weight of barium sulphate = 0.466g
Formula used:
Percentage of S = $\frac{32}{233}\times\frac{x}{w}\times 100$
Solution:
Percentage of S = $\frac{32}{233}\times\frac{x}{w}\times 100$
Percentage of S = $\frac{32}{233}\times\frac{0.466}{0.32}\times 100$

Percentage of S =20%

50. 0.24g of an organic compound gave 0.287 g of silver chloride in the carius method. Calculate the percentage of chlorine in the compound.
Given:
Weight of organic compound = 0.24g
Weight of silver chloride = 0.287g
Formula used:
Percentage of Cl = $\frac{35.5}{143.5}\times\frac{x}{w}\times 100$
Solution:
Percentage of Cl = $\frac{35.5}{143.5}\times\frac{x}{w}\times 100$
Percentage of Cl = $\frac{35.5}{143.5}\times\frac{0.287}{0.24}\times 100$

Percentage of Cl = 29.42%

51. In the estimation of nitrogen present in an organic compound by Dumas method 0.35g yielded 20.7 mL of nitrogen at 15° C and 760 mm pressure. Calculate the percentage of nitrogen in the compound.
Given:
Weight of the organic compound = 0.35g
V_1 = 20.7ml = 20.7×10^{-3}L
T_1 = 15°C = 288K
P_1 = 760mmHg

Formula used:

Percentage of N by Dumas method = $\frac{28}{22.4} \times \frac{v_o}{w} \times 100$

Solution:

$$\frac{P_o V_o}{T_0} = \frac{P_1 V_1}{T_1}$$

$$V_o = \frac{P_1 V_1}{T_1} \frac{T_o}{P_o}$$

$$V_o = \frac{760 \times 20.7 \times 10^{-3}}{288} \times \frac{273}{760}$$

$V_o = 19.62 \times 10^{-3}$ L

Percentage of N by Dumas method = $\frac{28}{22.4} \times \frac{v_o}{w} \times 100$

Percentage of N by Dumas method = $\frac{28}{22.4} \times \frac{19.62 \times 10^{-3}}{0.35} \times 100$

Percentage of N by Dumas method = 7.007%