NEET JEE ESSENTIALS

Class



Maximise your chance of success, and high rank in NEET, JEE (Main and Advanced) by reading this column. This specially designed column is updated year after year by a panel of highly qualified teaching experts well-tuned to the requirements of these Entrance Tests.

Unit 7

Organic Chemistry — Some Basic Principles and Techniques

INTRODUCTION

Organic chemistry is the chemistry of carbon compounds as all organic compounds contain carbon as their essential constituent. Organic compounds may be regarded as hydrocarbons *i.e.*, compounds of carbon and hydrogen only. A large number of organic compounds also contain elements like N, O, S, X, etc. which are derived from hydrocarbons by replacing one or more hydrogen atoms in their molecules with these atoms. Thus, the modern definition of the organic chemistry is "the chemistry of the hydrocarbons and their derivatives."

ORGANIC COMPOUNDS

Tetravalency of Carbon

Carbon can complete its octet by sharing its valence electrons with the electrons of other atoms, by virtue of

which it forms four covalent bonds, is generally referred to as tetracovalency of carbon. The unique capacity of carbon atom to form bonds with other carbon atoms, is called catenation.

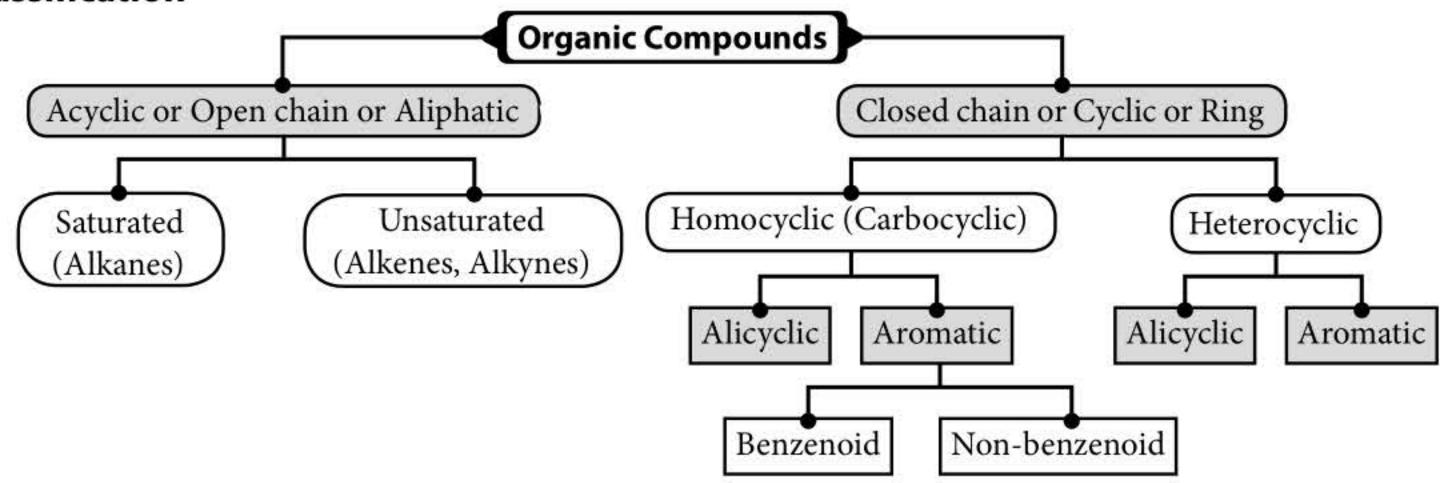
Shapes

| Type of hybridisation | Orbitals used | Geometry of the hybrid orbitals formed | Bond angle | Percentage of <i>s</i> - and <i>p</i> -characters |
|--------------------------|------------------|-------------------------------------------------|---------------|---------------------------------------------------------|
| sp ³ | one s + three p | Tetrahedral | 109.5° | 25% s + 75% p |
| sp ² | one s + two p | Trigonal planar | 120° | 33.3% s + 66.7% p |
| sp | one s + one p | Linear | 180° | 50% s + 50% p |

Structural Representation

| Complete formula | Condensed formula | Bond-line formula | Polygon formula | 3D Representation |
|---------------------|--------------------------------------------|-------------------|--------------------|-------------------------------------------------------------------------------------------------------------------|
| H H | CH ₃ —CH ₃ Ethane | n-Pentane | Cyclopropane | Bonds in the plane of paper H C Dashed wedge (bond away from observer) H Solid wedge (bond towards observer) |





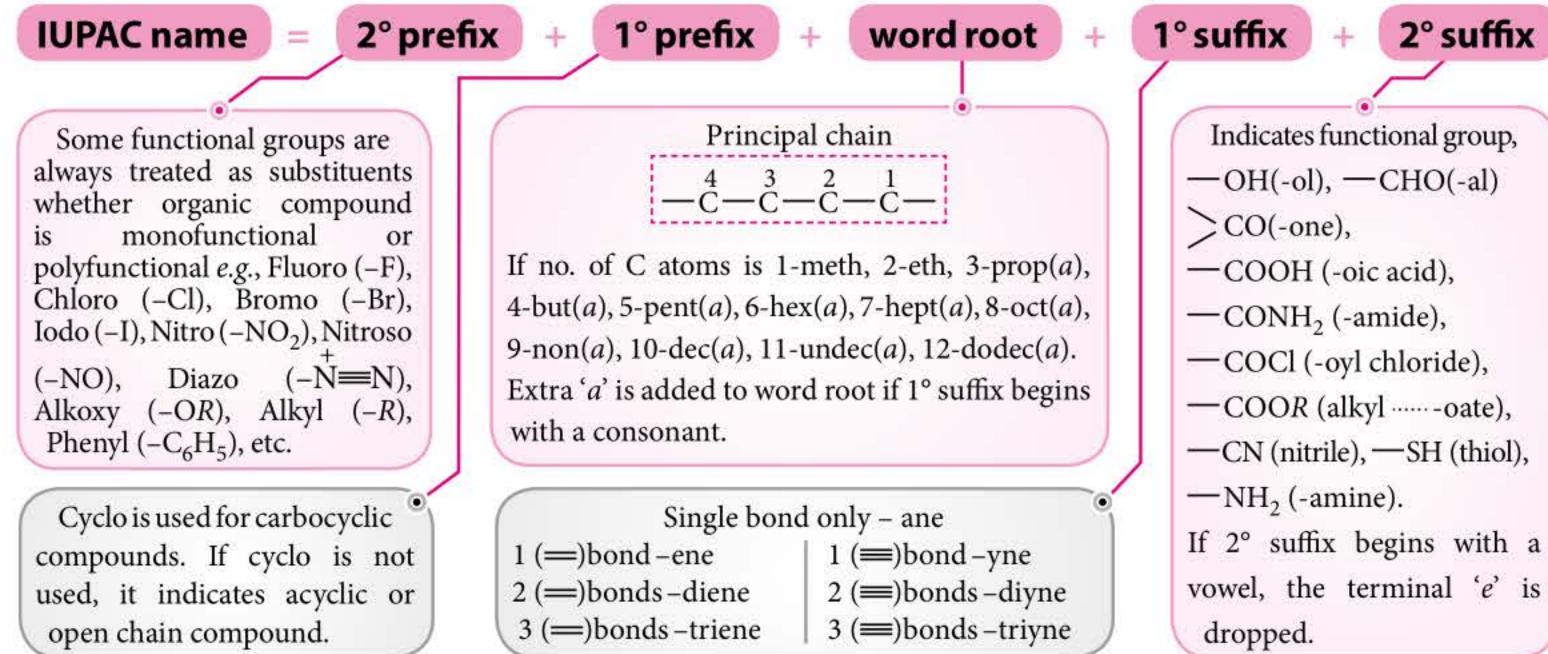
Homologous Series

A series of organic compounds, each containing a characteristic functional group, forms a homologous series in which each successive member differs by a $-CH_2$ unit or by $12 + 2 \times 1 = 14$ mass units.

Functional Groups

An atom or a group of atoms joined in a specific manner which is responsible for the characteristic chemical properties of the organic compounds *e.g.*, hydroxyl group (—OH), aldehyde group (—CHO), carboxylic acid group (—COOH), etc.

IUPAC Nomenclature



| Compound | IUPAC name | Compound | IUPAC name |
|-----------------------------------------------------------------|---------------|-----------------------------------------------------------------|----------------------|
| CH ₃ CH ₂ CH ₂ CH ₃ | Butane | CH ₃ CH ₂ OH | Ethanol |
| СН≡СН | Ethyne | CH ₃ CH ₂ CH ₂ NH ₂ | Propanamine |
| CH ₃ COOH | Ethanoic acid | НС≡ССООН | Prop-2-yn-1-oic acid |
| CH ₃ CH ₂ Br | Bromoethane | CH ₃ CH ₂ COCH ₃ | Butan-2-one |
| C ₂ H ₅ OC ₂ H ₅ | Ethoxyethane | CH ₃ | 2-Methylpropane |
| | | CH ₃ -CH-CH ₃ | |

| CH ₃ CH ₃ | 1, 2-Dimethylcyclopentane | | Cyclohexene |
|---------------------------------|---------------------------|----------------------|------------------------|
| OH CH ₃ | 2-Methylphenol | O_2N NO_2 NO_2 | 2, 4, 6-Trinitrophenol |

Isomerism

The phenomenon of existence of two or more compounds possessing the same molecular formula but different properties is known as isomerism. It is classified broadly into structural isomerism and stereoisomerism.

Types of structural isomerism:

| Isomerism | Description | Example |
|-----------------------|----------------------------------------------------------------------------------------------------------------------------------------------------|---------------------------------------------------------------------------------------------------------------------|
| Chain isomerism | Arises due to different arrangements of C-atoms. The chain isomers have almost similar chemical properties but different physical properties. | CH_3 $H_3C-CH_2-CH_2-CH_3$, $H_3C-CH-CH_2$ Butane Isobutane |
| Position isomerism | Arises due to different positions of side chains, substituents, functional groups, double bonds, triple bonds, etc. on the parent chain. | $H_2C = CH - CH_2 - CH_3$, $But-1-ene$ $H_3C - CH = CH - CH_3$ $But-2-ene$ |
| Functional isomerism | Arises due to presence of different functional groups. These isomers differ in both physical and chemical properties. | ■ 전 |
| Metamerism | Arises due to different alkyl groups on either side of the functional group. | $H_3C-CH_2-O-CH_2-CH_3$ Diethyl ether or Ethoxyethane $H_3C-O-CH_2-CH_2-CH_3$ Methyl propyl ether or Methoxypropane |
| Tautomerism | Tautomers have different functional groups and exist in dynamic equilibrium with each other due to rapid interconversion from one form to another. | O OH $H_3C-C-CH_3 \iff H_3C-C=CH$ Acetone Prop-1-en-2-ol (keto form) (enol form) Keto-enol tautomerism |



Antiaromatic molecules display record electrical conductance!

Antiaromatic compounds featuring planar rings of carbon atoms sharing a number of electrons that is a multiple of four, have been predicted to be excellent conductors. Researchers demonstrate high electrical conductance for an antiaromatic nickel complex-an order of magnitude higher than for a similar aromatic complex. Since, the conductance is also tunable by electrochemical gating, antiaromatic complexes are promising materials for future electronic devices.

Types of stereoisomerism:

Isomers have the same structural formula but differ in the spatial arrangement of atoms or Geometrical isomerism groups of atoms about double bond. (Similar groups on the different (Similar groups on the same Compounds containing C=N and N=Nside of the double bond) sides of the double bond) bonds also show geometrical isomerism. In these cases, 'syn' (for cis) and 'anti' (for trans) are more commonly used. E and Z system of nomenclature is used for highly substituted alkenes, having four different atoms or groups, attached to C = C bond. *E* is assigned to an isomer in which high priority atoms or groups are on the opposite sides. Z is assigned to an isomer in which high priority atoms or groups are on the same side. Compounds having similar physical and chemical properties but differing only in the behaviour towards polarised light are called optical isomers and the phenomenon is called optical isomerism. Some substances have the ability to rotate the plane polarised light either to the right (clockwise) i.e., dextrorotatory or to the left (anticlockwise) i.e., laevorotatory are optically active substances and the property is called optical activity. In order to exhibit optical activity, an object must be chiral. The compound is said to have chirality if the central carbon atom E is attached to four different groups and this centre is called chiral Optical isomeris (asymmetric) centre or stereogenic centre or stereocentre. Achiral centre Chiral centre If the central carbon atom has at least two identical groups then this (asymmetric) (symmetric) centre is called achiral (symmetric) centre. If molecule has a plane of symmetry, it is achiral and if molecule has no plane of symmetry, it is chiral. Enantiomers or d-and l-isomers are the optical isomers which are non-superimposable mirror images (or dissymmetric). Equimolecular mixture of d- and l-forms is known as racemic mixture (dl-form). This is optically inactive due to external compensation. Diastereomers are the optical isomers which are not mirror images of each other. They have different

FUNDAMENTAL CONCEPTS IN REACTION MECHANISM

physical properties and magnitude of specific rotation.

Reaction Intermediates

| Intermediates | Definition | Hybridisation of carbon and shape | Stability order |
|--------------------------------------------------------------------------------------------------------------------------------------|----------------------------|-----------------------------------|-----------------|
| Carbocation: Formed by heterolytic cleavage of the covalent bond in which the leaving group takes away the shared pair of electrons. | | | 3° > 2° > 1° |
| Carbanion: Formed by heterolytic cleavage of the covalent bond in which the shared pair of electrons remains with the carbon atom. | negative charge on carbon. | | 1° > 2° > 3° |

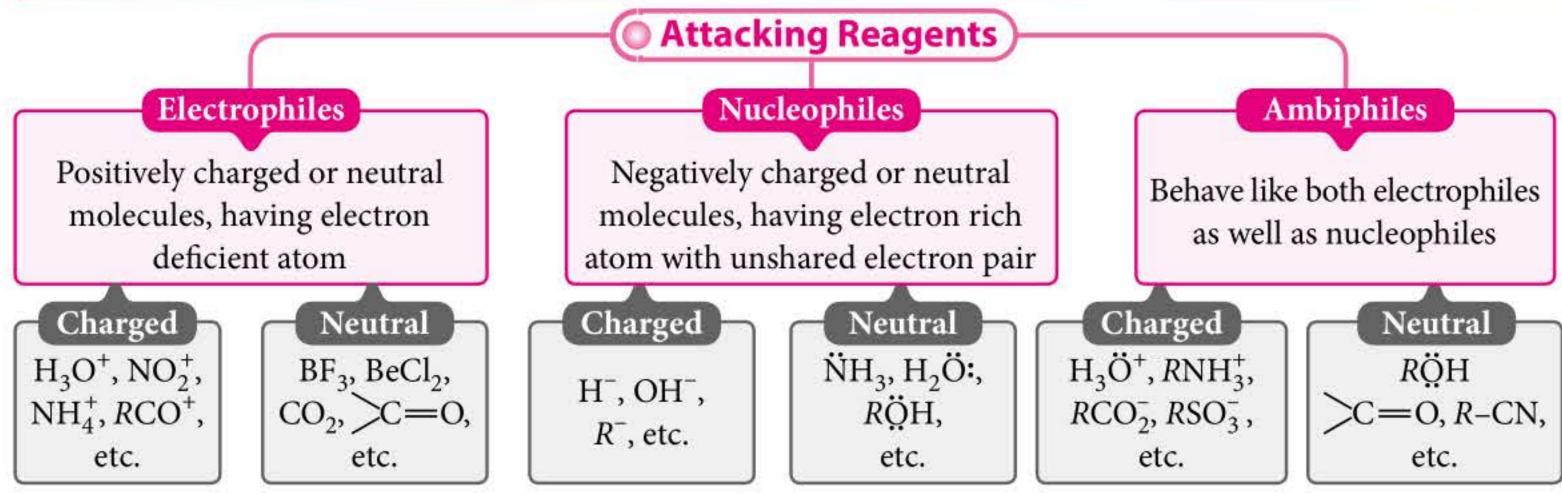
Meso compounds are those compounds which have two or more even number of chiral carbon atoms and

have an internal plane of symmetry. They are optically inactive due to internal compensation.

Free radical: Formed by homolytic cleavage of a covalent bond.

Atom or group of atoms having odd or unpaired electrons. sp^2 -Hybridised carbon and trigonal planar shape. sp^2 -Hybridised carbon and trigonal planar shape.

ATTACKING REAGENTS



ELECTRON DISPLACEMENT EFFECTS IN COVALENT BOND

-I effect: R_3N- , $-NO_2$, $-SO_2R$, -CN, -COOH, -F, -Cl, Inductive effect: Displacement of σ-electrons along a saturated carbon chain $-Br, -I, -OR, -COR, -OH, -C_6H_5, -CH = CH, etc.$ when an electron donating (+I effect) or +I effect: $(CH_3)_3C-$, $(CH_3)_2CH-$, CH_3CH_2- , CH_3- , electron withdrawing (-I effect) group is $-COO^-$, etc. attached at the end of the carbon chain. **Electromeric effect :** It involves complete +*E* effect: When electron transfer takes place towards the atom transfer of π -electrons of a multiple bond to which the attacking reagent gets attached. towards one of the bonded atoms in the -E effect: When electron transfer takes place away from the presence of an attacking reagent. atom to which the attacking reagent gets attached. +R effect: -Cl, -Br, -I, $-NH_2$, -NHR, $-NR_2$, Resonance or mesomeric effect : It is defined as the polarity produced in -NHCOR, -OH, -OR, -SR, -SH, $-OCH_3$, -OCOR, etc. the molecule by the interaction of two -R effect: $-NO_2$, -CN, -CHO, -COOH, -COR, etc. π -bonds or between a π -bond and a lone pair of electrons present on adjacent atom. Hyperconjugation: It involves delocali-For an alkyl group attached to unsaturated system, it decreases sation of σ-electrons of C—H bond of an with decrease in number of α -hydrogens : alkyl group directly attached to an atom of $CH_3 - > CH_3CH_2 - > (CH_3)_2CH - > (CH_3)_3C$ unsaturated system or to an atom having vacant *p*-orbital.

METHODS OF PURIFICATION OF ORGANIC COMPOUNDS

| Method | Used for separating | Examples | |
|-----------------|-----------------------------------------------------------------------------------------------------|-----------------------------------------------------------------------------|-----|
| Crystallisation | Mixtures with difference in the solubility of the organic compound and its impurities in a solvent. | be crystallised from hot ethanol at 34 (sugar dissolves but salt does not). | 8 K |

| Sublimation | Mixtures of sublimable volatile compounds and non-sublimable impurities. | Purification of camphor, anthracene, naphthalene, benzoic acid, etc. |
|-------------------------|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|----------------------------------------------------------------------------------------------------------------------------------------|
| Simple distillation | Mixtures of liquids having sufficient difference in their boiling points and contain non-volatile impurities. | Chloroform (b.pt. 334 K) and aniline (b.pt. 457 K). Ether (b.pt. 308 K) and toluene (b.pt. 384 K). |
| Fractional distillation | Mixtures of two or more miscible liquids which have b.pt. close to each other. | Acetone (b.pt. 329 K) and methyl alcohol (b.pt. 338 K). Benzene (b.pt. 353 K) and toluene (b.pt. 383 K). |
| Steam distillation | Mixtures of substances which are (i) volatile in steam, (ii) not miscible with water, (iii) possess a vapour pressure of about 10-15 mm of Hg, and (iv) contain non-volatile impurities. | Aniline and water. Purification of nitrobenzene, o-nitrophenol, bromobenzene, etc. |
| Azeotropic distillation | Mixtures with constant boiling points <i>i.e.</i> , azeotropic mixtures. | • Ethanol and water in ratio 95.87 : 4.13. |
| Vacuum distillation | Mixtures of high boiling liquids which decompose at or below their boiling points. | Glycerol from spent-lye in soap industry (at 453 K under 12 mm Hg). Concentration of sugarcane juice. |
| Chromatography | Mixtures with difference in the rates at which the components of the mixture move through a porous medium. | ortho and para nitroaniline. Blue and red dyes. Plant pigments and other natural products. |
| Differential extraction | Mixtures of organic compounds from their aqueous solutions using a solvent that should (i) be immiscible with water, (ii) dissolve the organic compound. | Benzoic acid from its aqueous solution using benzene. |

QUALITATIVE ANALYSIS OF ORGANIC COMPOUNDS

| Element | Detection | Confirmatory test | Reaction |
|----------|----------------------------------------------------------------------------------------------------------|----------------------------------------------------------------------------------------------------------------|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| Carbon | Copper(II) oxide test $2\text{CuO} + \text{C} \xrightarrow{\Delta} 2\text{Cu} + \text{CO}_2 \uparrow$ | CO ₂ gas turns lime water milky. | $CO_2 + Ca(OH)_2 \rightarrow CaCO_3 \downarrow + H_2O$ Lime water Milkiness |
| Hydrogen | $CuO + 2H \xrightarrow{\Delta} Cu + H_2O$ | Water droplets appear on the cooler part of the ignition tube and also turns anhydrous CuSO ₄ blue. | $CuSO_4 + 5H_2O \rightarrow CuSO_4 \cdot 5H_2O$ White Blue |
| Nitrogen | Lassaigne's extract (L.E.) Na + C + N $\xrightarrow{\Delta}$ NaCN (L.E.) | L.E. + FeSO ₄ + NaOH, boil and cool + FeCl ₃ + conc. HCl → blue or green colour. | $\begin{aligned} \text{FeSO}_4 + 2\text{NaOH} &\rightarrow \\ \text{Fe(OH)}_2 + \text{Na}_2\text{SO}_4 \\ \text{Fe(OH)}_2 + 6\text{NaCN} &\rightarrow \\ \text{Na}_4[\text{Fe(CN)}_6] + 2\text{NaOH} \\ 3\text{Na}_4[\text{Fe(CN)}_6] + 4\text{FeCl}_3 &\rightarrow \\ \text{Fe}_4[\text{Fe(CN)}_6]_3 + 12\text{NaCl} \\ \text{Prussian blue} \end{aligned}$ |

| Sulphur | $2Na + S \xrightarrow{\Delta} Na_2S$ (L.E.) | L.E. + sodium nitroprusside → deep violet colour. L.E. + CH₃COOH + (CH₃COO)₂Pb → black ppt. | $Na_2S + Na_2[Fe(CN)_5NO] \rightarrow Sodium nitroprusside Na_4[Fe(CN)_5NOS]Deep violetNa_2S + (CH_3COO)_2Pb \xrightarrow{CH_3COOH} PbS \downarrow + 2CH_3COONaBlack ppt.$ |
|-------------------------------------|-----------------------------------------------------------------------|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| Halogens | Na + $X \xrightarrow{\Delta}$ Na X (L.E.) | L.E. + HNO₃ + AgNO₃, if white ppt. soluble in aq. NH₃ (or NH₄OH) confirms Cl. dull yellow ppt. partially soluble in aq. NH₃ (or NH₄OH) confirms Br. yellow ppt. insoluble in aq. NH₃ (or NH₄OH) confirms I. | $NaX + AgNO_3 \xrightarrow{HNO_3} AgX \downarrow$ $ppt.$ $AgCl + 2NH_{3(aq.)} \rightarrow [Ag(NH_3)_2]Cl$ White Soluble ppt. $AgBr + 2NH_{3(aq.)} \rightarrow [Ag(NH_3)_2]Br$ Dull Partially soluble yellow ppt. $AgI + 2NH_{3(aq.)} \rightarrow [Ag(NH_3)_2]I$ Yellow Insoluble ppt. |
| Nitrogen and sulphur together | Na + C + N + S $\xrightarrow{\Delta}$ NaSCN Sodium thiocyanate (L.E.) | As in test for nitrogen; instead of green or blue colour, blood red colouration confirms presence of N and S both. | ACCUSED AND STREET STREET STREET STREET |
| Phosphorus | $P \xrightarrow{Na_2O_2, boil} Na_3PO_4$ | Solution is boiled with nitric acid and then treated with ammonium molybdate $(NH_4)_2MoO_4$. Formation of yellow ppt. indicates the presence of phosphorus in organic compound. | $H_3PO_4 + 3NaNO_3$ $H_3PO_4 + 12(NH_4)_2MoO_4$ $+ 21HNO_3$ |

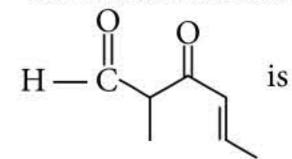
QUANTITATIVE ANALYSIS OF ORGANIC COMPOUNDS

| Element | Method | | |
|----------|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|--|--|
| | Liebig's combustion method: % of $C = \frac{12}{44} \times \frac{\text{mass of CO}_2 \text{ formed}}{\text{mass of compound taken}} \times 100$ % of $H = \frac{2}{18} \times \frac{\text{mass of H}_2\text{O formed}}{\text{mass of compound taken}} \times 100$ | | |
| Nitrogen | Dumas method: % of $N = \frac{28}{22400} \times \frac{\text{vol. of N}_2 \text{ at STP}}{\text{mass of compound taken}} \times 100$ Kjeldahl's method: | | |
| | % of N = $\frac{1.4 \times \text{molarity of acid} \times \text{vol. of acid used} \times \text{basicity of acid}}{\text{mass of compound taken}}$ | | |

| Halogens | Carius method: % of $X = \frac{\text{At. mass of } X}{108 + \text{At. mass of } X} \times \frac{\text{mass of Ag}X \text{ formed}}{\text{mass of compound taken}} \times 100$ |
|------------|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| Sulphur | Carius method: % of $S = \frac{32}{233} \times \frac{\text{mass of BaSO}_4 \text{ formed}}{\text{mass of compound taken}} \times 100$ |
| Phosphorus | Ignition method: % of $P = \frac{62}{222} \times \frac{\text{mass of Mg}_2 P_2 O_7 \text{ formed}}{\text{mass of compound taken}} \times 100$ |
| Oxygen | Iodine method: $\% \text{ of } O = \frac{16}{44} \times \frac{\text{mass of CO}_2 \text{ formed}}{\text{mass of compound taken}} \times 100 \text{ or } \% \text{ of } O = \frac{5 \times 16}{2 \times 127} \times \frac{\text{mass of I}_2 \text{ formed}}{\text{mass of compound taken}} \times 100$ |



- 1. In Lassaigne's test for nitrogen, the blue colour is due to the formation of
 - (a) ferric ferrocyanide
 - (b) potassium ferrocyanide
 - (c) sodium ferrocyanide
 - (d) sodium cyanide.
 - . The IUPAC name of the compound \bigvee i
 - (a) 3,4-dimethyl-1-penten-3-ol
 - (b) isopropyl-3-methylvinylcarbinol
 - (c) 2,3-dimethyl-4-penten-3-ol
 - (d) none of the above.
- 3. The number of structural isomers for C_6H_{14} is
 - (a) 3
- (b) 4
- (c) 5
- (d) 6
- 4. The IUPAC name of the compound



- (a) 5-formylhex-2-en-3-one
- (b) 5-methyl-4-oxohex-2-en-5-al
- (c) 3-keto-2-methylhex-5-enal
- (d) 3-keto-2-methylhex-4-enal.

(NEET 2017)

- 5. The Lassaigne's extract is boiled with conc. HNO₃ while testing for halogens. Because it
 - (a) decomposes Na₂S and NaCN, if formed

- (b) helps in the precipitation of AgCl
- (c) increases the solubility product of AgCl
- (d) increases the concentration of NO₃ ions.
- 6. Hyperconjugation is most useful for stabilising which of the following carbocations?
 - (a) Neopentyl
- (b) tert-Butyl
- (c) Isopropyl
- (d) Ethyl
- 7. Which of the following statements is not true about partition chromatography?
 - (a) Mobile phase can be a gas or liquid.
 - (b) Separation depends upon equilibration of solute between a mobile and a stationary phase.
 - (c) Stationary phase is a finely divided solid adsorbent.
 - (d) None of the above.
- The less reactivity of chlorine atom in, CH₂ = CH—Cl is due to
 - (a) inductive effect
- (b) resonance stabilisation
- (c) electromeric effect
- (d) electronegativity.
- Among the following, the least stable resonance structure is

