

**CLASS-XI**

*for*

# BRUSH UP NEET/JEE

# 2020

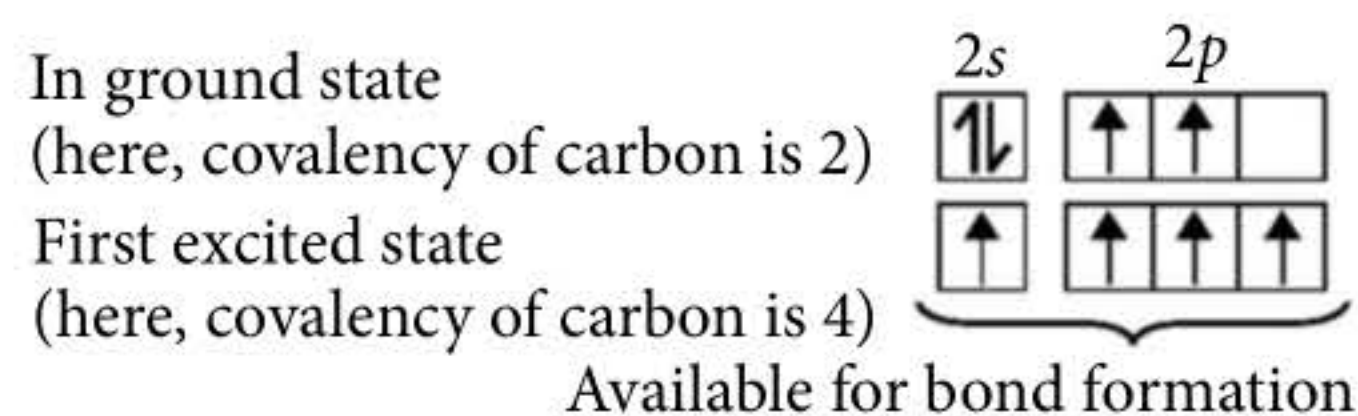
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Unit  
7

## Organic Chemistry-Some Basic Principles and Techniques

### Organic Chemistry-Some Basic Principles and Techniques

- Organic chemistry deals with the study of hydrocarbons (compounds of carbon and hydrogen elements) and other compounds regarded as derivatives of hydrocarbons. Some organic compounds may also contain nitrogen, oxygen, sulphur, phosphorus, halogens, etc.
- Reasons for existence of large number of organic compounds :**
  - Tetravalency :** Atomic number of carbon atom is 6 and it has four valence electrons so C-atom is tetravalent.
- Types of hybridisation of C-atom :**



- Catenation :** The property of atoms of an element to link with one another forming chains of identical atoms is called catenation. Carbon exhibits catenation to the maximum extent.
- Formation of multiple bonds :** Because of its small size carbon atom is capable of forming multiple bonds with other atoms and this gives a variety of compounds.

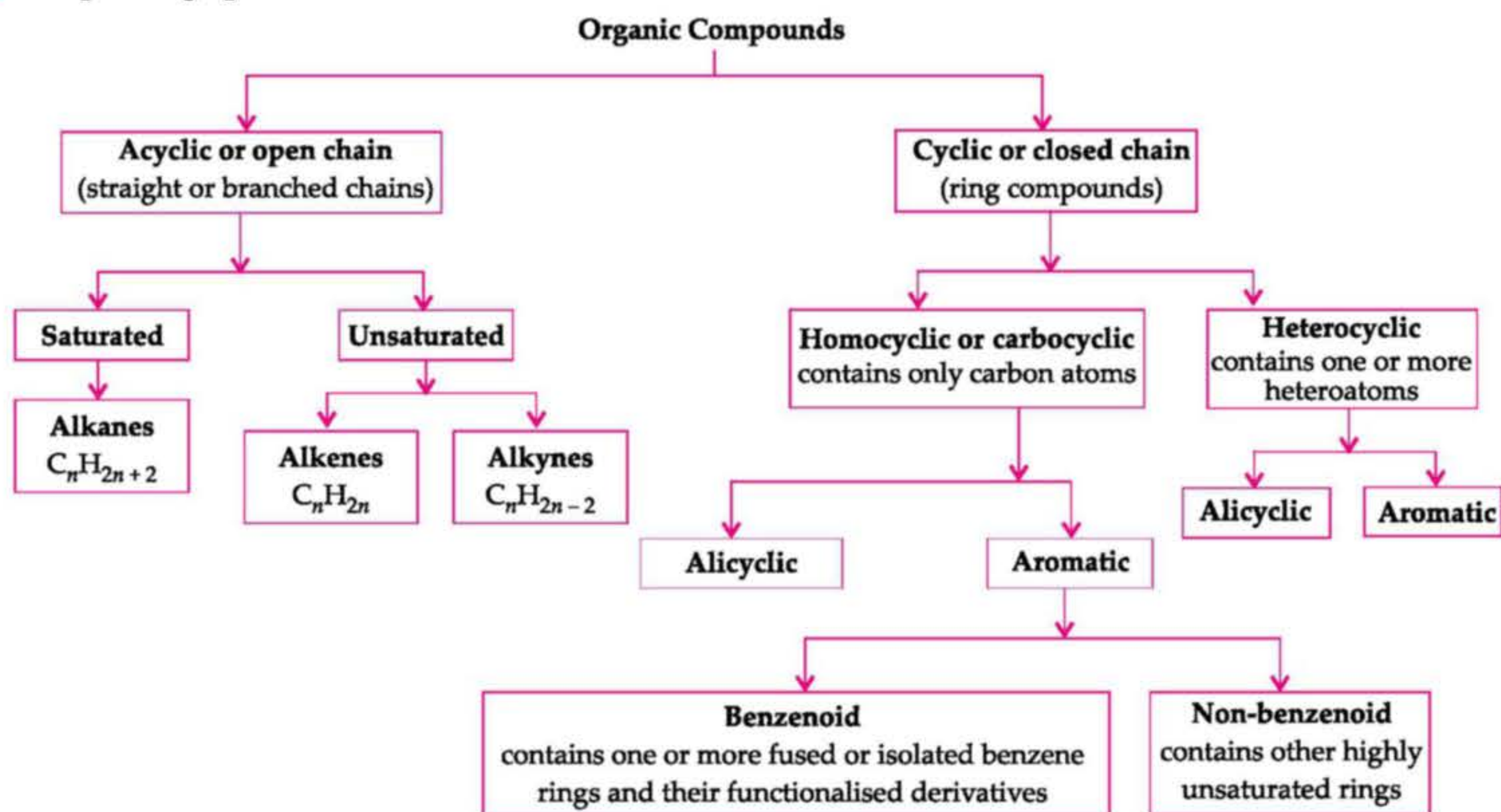
Hybridisation	Participating orbitals	Number of equivalent orbitals formed	Unhybridised orbitals	Structuret	Bond angle	Examples
$sp^3$	one $s$ and three $p$	4	0	Tetrahedral	$109^{\circ}28'$	Ethane, methane
$sp^2$	one $s$ and two $p$	3	1	Trigonal planar	$120^{\circ}$	Ethene, propene
$sp$	one $s$ and one $p$	2	2	Linear	$180^{\circ}$	Ethyne, propyne



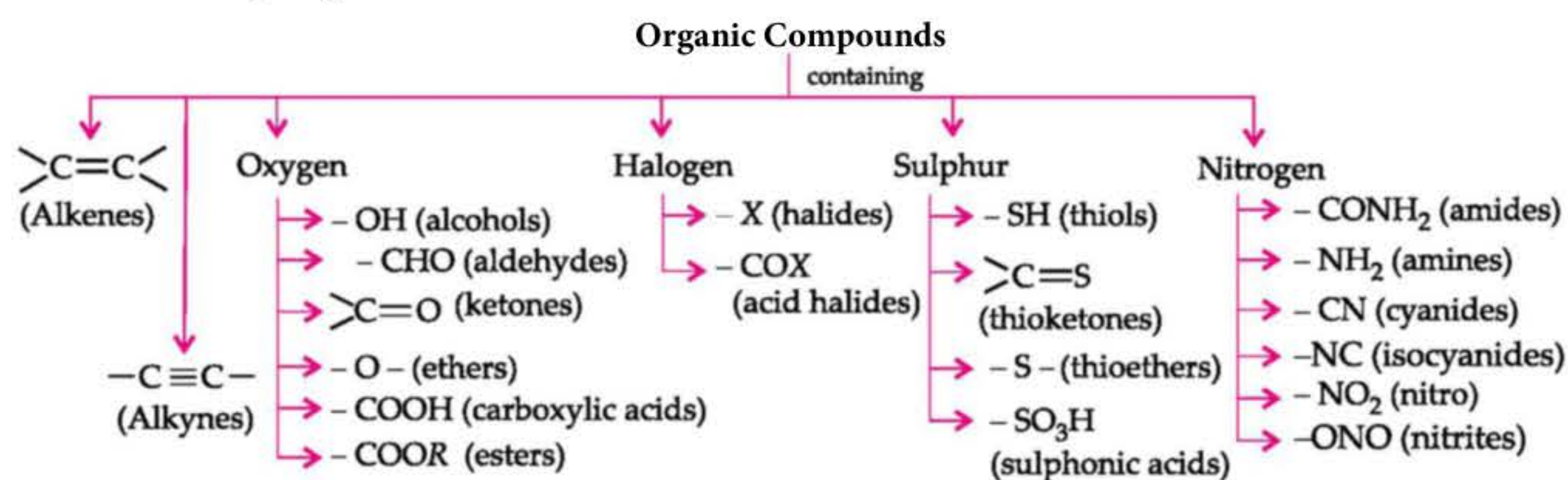
## CLASSIFICATION OF ORGANIC COMPOUNDS

Organic compounds are broadly classified into following categories:

- Depending upon the nature of their carbon skeleton:



- Based on functional groups :



- Homologous series :** A series of organic compounds where preceding or succeeding members differ by one  $-\text{CH}_2$  group is called homologous series and the members are called homologues.
- Characteristics of a homologous series :**
  - Difference in the molecular masses of two successive homologues is 14 ( $\text{CH}_2 = 12 + 2 \times 1 = 14$ ).
  - They are represented by a general molecular formula :
- Members of the homologous series can be prepared by the general methods of preparation developed for that series.
- They show regular gradation in physical properties.
- They have almost similar chemical properties.

Alkanes	$\text{C}_n\text{H}_{2n+2}$
Alkenes	$\text{C}_n\text{H}_{2n}$
Alkynes	$\text{C}_n\text{H}_{2n-2}$

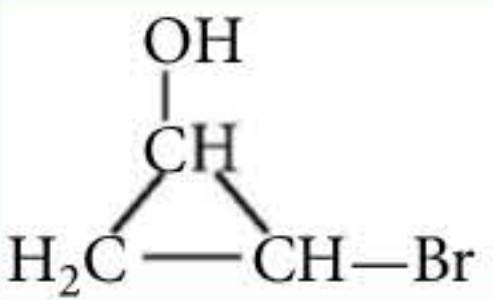
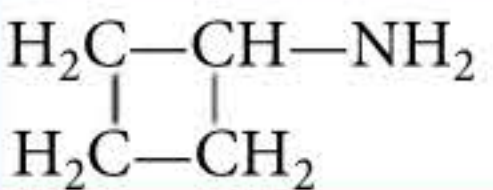
## NOMENCLATURE OF ORGANIC COMPOUNDS

IUPAC name of an organic compound has the following arrangement.

Secondary prefix + Primary prefix + Word root + Primary suffix + Secondary suffix



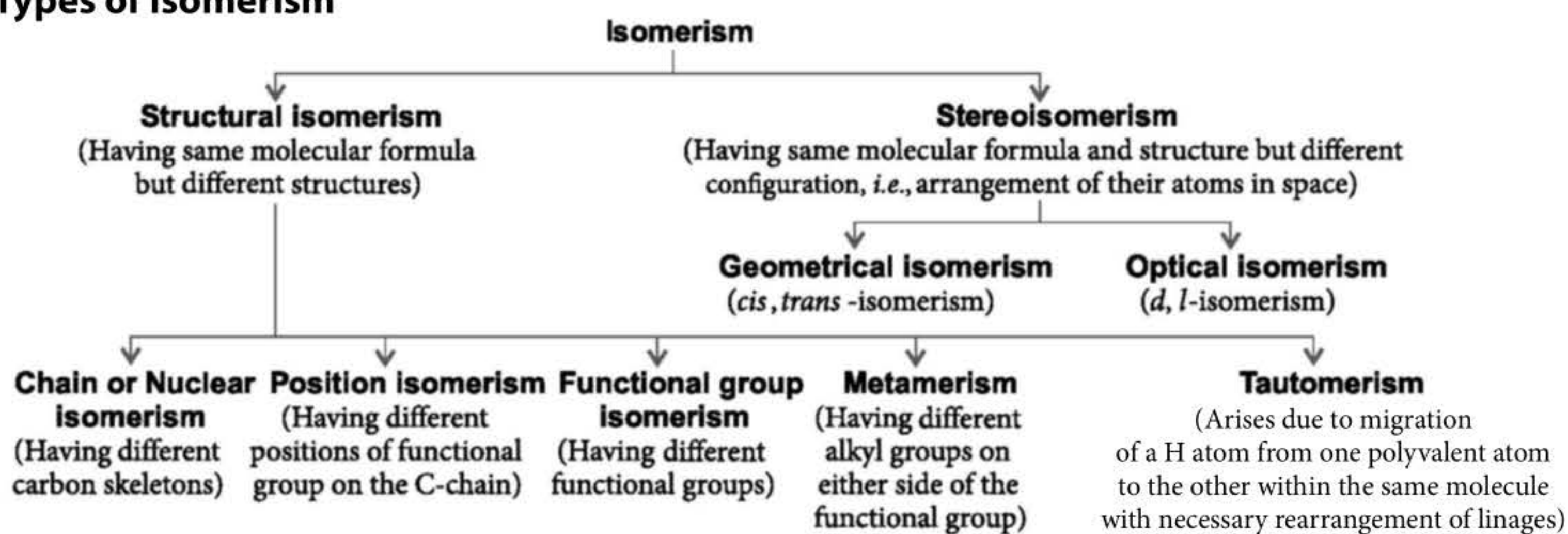
For example,

Organic compound	Secondary prefix	Primary prefix	Word root	Primary suffix	Secondary suffix	IUPAC name
	Bromo	Cyclo	Prop	ane	ol	Bromocyclopropanol
CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> OCH <sub>3</sub>	Methoxy	-	Prop	ane	-	Methoxypropane
	-	Cyclo	But	ane	amine	Cyclobutanamine

## ISOMERISM

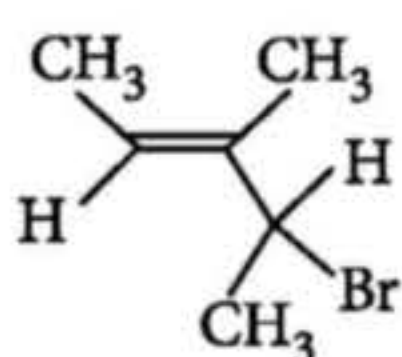
It is the property by virtue of which two or more compounds have the same molecular formula but different physical or chemical properties.

### Types of Isomerism



### PEEP INTO PREVIOUS YEARS

1. What is the IUPAC name of the following compound?



- (a) 4-Bromo-3-methylpent-2-ene  
 (b) 2-Bromo-3-methylpent-3-ene  
 (c) 3-Bromo-3-methyl-1,2-dimethylprop-1-ene  
 (d) 3-Bromo-1,2-dimethylbut-1-ene

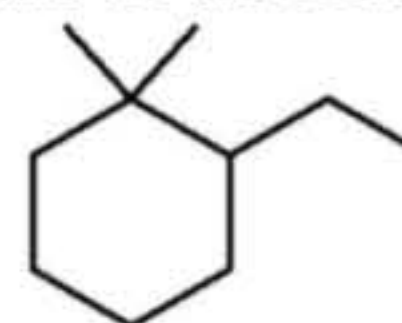
(JEE Main 2019)

2. Which of the following molecules represents the order of hybridisation  $sp^2, sp^2, sp, sp$  from left to right atoms?

- (a)  $\text{HC} \equiv \text{C} - \text{C} \equiv \text{CH}$   
 (b)  $\text{CH}_2 = \text{CH} - \text{C} \equiv \text{CH}$   
 (c)  $\text{CH}_2 = \text{CH} - \text{CH} = \text{CH}_2$   
 (d)  $\text{CH}_3 - \text{CH} = \text{CH} - \text{CH}_3$

(NEET 2018)

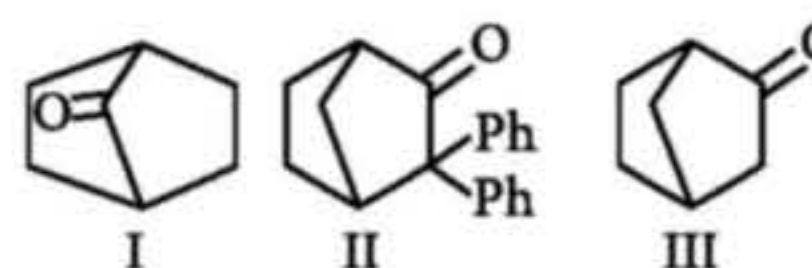
3. The IUPAC name of the following compound is



- (a) 1-ethyl-2, 2-dimethylcyclohexane  
 (b) 2, 2-dimethyl-1-ethylcyclohexane  
 (c) 1, 1-dimethyl-2-ethylcyclohexane  
 (d) 2-ethyl-1, 1-dimethylcyclohexane.

(JEE Main 2017)

4. Which among the given molecules can exhibit tautomerism?



- (a) III only  
 (b) Both I and III  
 (c) Both I and II  
 (d) Both II and III

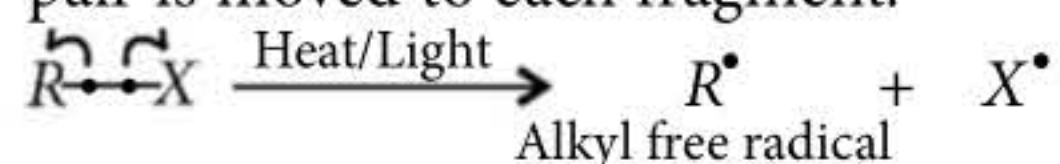
(NEET-II 2016)



## FUNDAMENTAL CONCEPTS IN ORGANIC REACTION MECHANISM

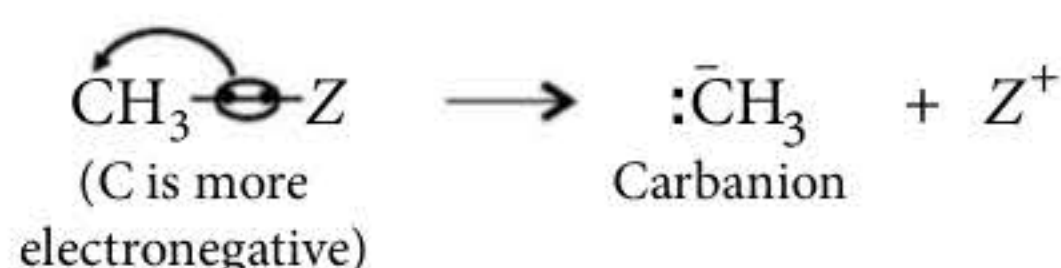
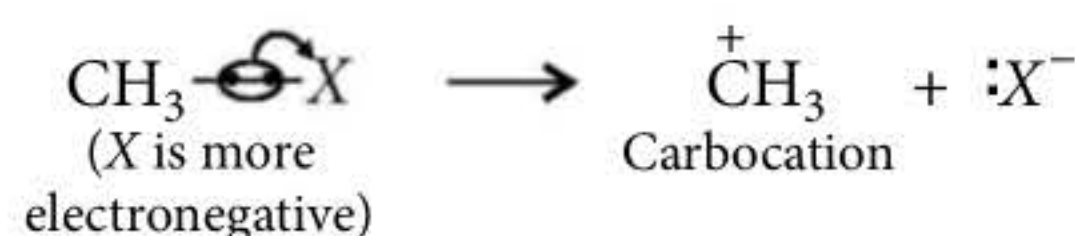
### Fission of a covalent bond :

- **Homolytic fission (symmetrical)** : Free radicals are formed by homolytic cleavage of covalent bond in which one of the electrons of the shared pair is moved to each fragment.



- **Heterolytic fission (unsymmetrical)** : Positive and negative ions are formed by heterolytic

cleavage of covalent bond in which both the electrons of the bonding pair are moved to one of the fragments (*i.e.*, towards more electronegative atom).



### Reaction Intermediates

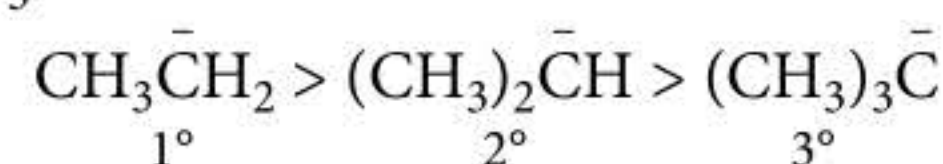
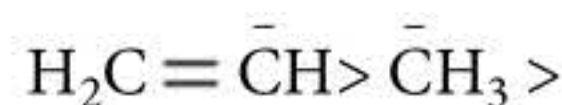
Intermediates	Definition	Hybridisation of carbon and shape	Stability order
Carbocation	Carbon species carrying +ve charge on carbon.	$sp^2$ hybridised carbon and planar structure.	$3^\circ > 2^\circ > 1^\circ$
Carbanion	Carbon species carrying -ve charge on carbon.	$sp^3$ hybridised carbon and pyramidal shape.	$1^\circ > 2^\circ > 3^\circ$
Free radical	Atom or group of atoms having odd or unpaired electron.	$sp^2$ hybridised carbon and planar structure.	$3^\circ > 2^\circ > 1^\circ$

### Relative stabilities of carbocation :

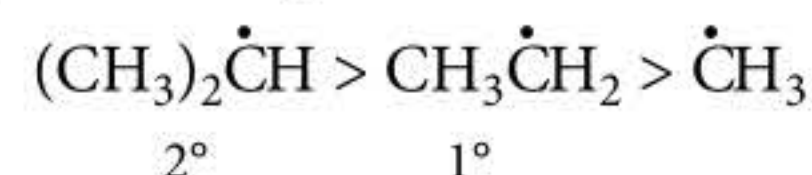
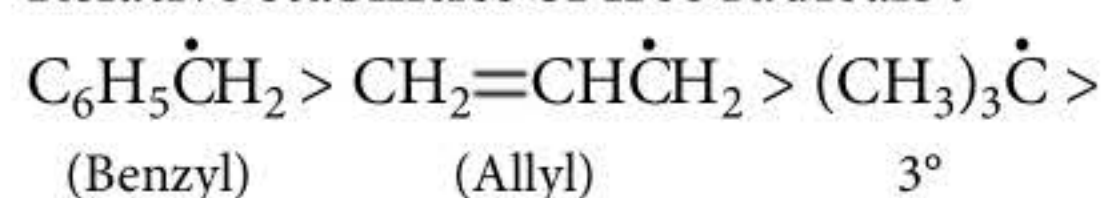
- $\text{CH}_3\text{CH}_2\text{CH}_2\overset{+}{\text{C}}\text{H}_2 > \text{CH}_3\text{CH}_2\overset{+}{\text{C}}\text{H}_2 > \text{CH}_3\overset{+}{\text{C}}\text{H}_2 > \overset{+}{\text{C}}\text{H}_3$
- $\text{Ph}_3\overset{+}{\text{C}} > \text{Ph}_2\overset{+}{\text{C}}\text{H} > (\text{CH}_3)_3\overset{+}{\text{C}} > \text{Ph}\overset{+}{\text{C}}\text{H}_2 > (\text{CH}_3)_2\overset{+}{\text{C}}\text{H} > \text{C}_6\text{H}_5^+ > \overset{+}{\text{C}}\text{H}_3 > \text{HC}\equiv\overset{+}{\text{C}}$

### Relative stabilities of carbanions :

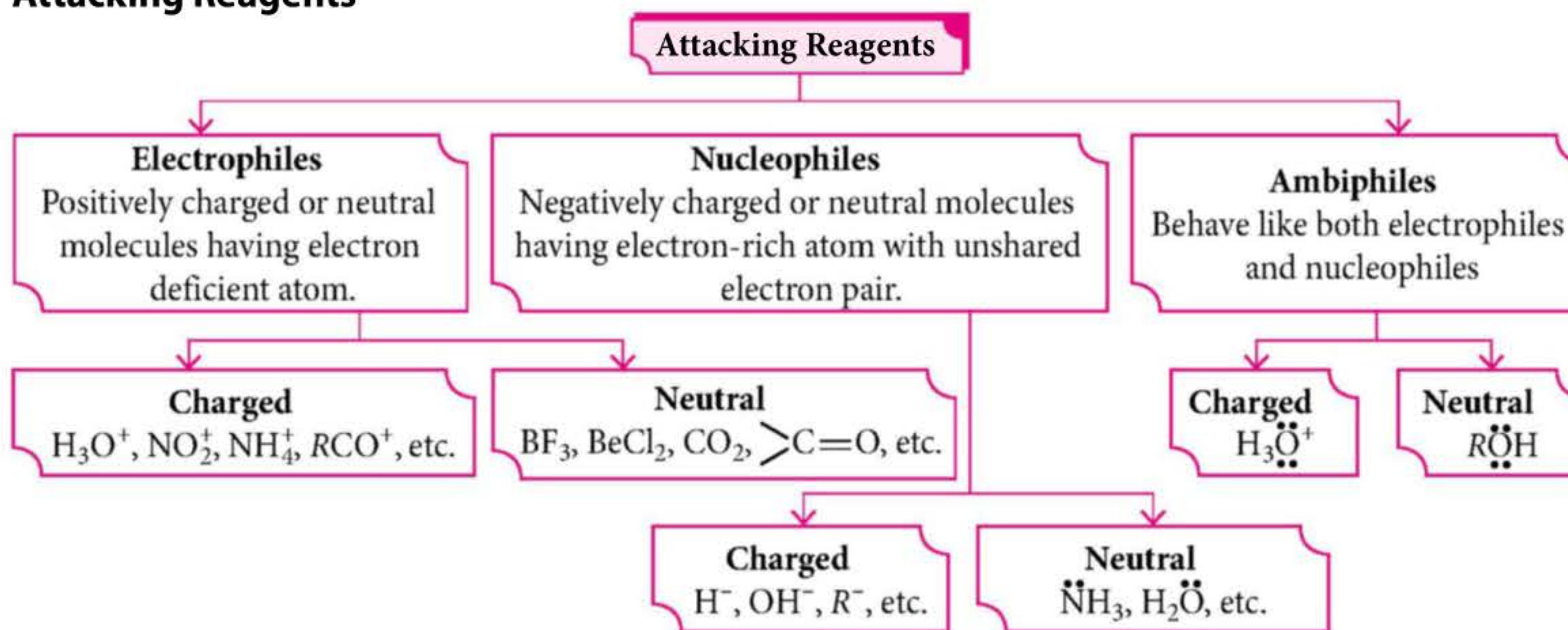
- $\text{HC}\equiv\text{C}^- > (\text{C}_6\text{H}_5)_3\text{C}^- > (\text{C}_6\text{H}_5)_2\text{CH}^- > \text{C}_6\text{H}_5\text{CH}_2^- > \text{CH}_2=\text{CH}-\text{CH}_2^- > \text{C}_6\text{H}_5^- > \overset{-}{\text{C}}\text{H}_3$



### Relative stabilities of free radicals :



### Attacking Reagents





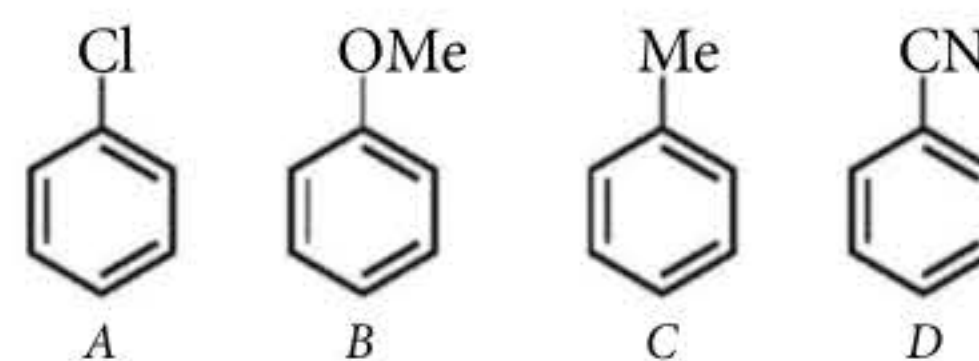
## Electron Displacement Effects in Covalent Bonds

- **Inductive effect (*I* effect)** : Displacement of  $\sigma$  electrons along a saturated carbon chain when an electron donating (+*I* effect) or electron withdrawing (–*I* effect) group is attached at the end of the carbon chain.
  - **Decreasing order of –*I* effect :**

$$R_3N^+ - > -NO_2 > -SO_2R > -CN > -COOH > -F > -Cl > -Br > -I > -OH > -OR > -CH=CH_2 > -C_6H_5 > -H$$
  - **Decreasing order of +*I* effect :**  $(CH_3)_3C - > (CH_3)_2CH - > CH_3CH_2 - > CH_3 - > D > H$
- **Electromeric effect (*E* effect)** : It involves complete transfer of  $\pi$  electrons of a multiple bond towards one of the bonded atoms in the presence of an attacking reagent.
  - **+*E* effect** : When electron transfer takes place towards the atom to which the attacking reagent gets attached.
  - **–*E* effect** : When electron transfer takes place away from the atom to which the attacking reagent gets attached.
- **Resonance or mesomeric effect** : It is defined as the polarity produced in the molecule by the interaction of two  $\pi$  bonds or between a  $\pi$  bond and a lone pair of electrons present on adjacent atom.
  - **+*R* or +*M* effect** :  $-Cl, -Br, -I, -NH_2, -NHR, -NR_2, -NHCOR, -OH, -OR, -SR, -SH, \text{ etc.}$
  - **–*R* or –*M* effect** :  $-NO_2, -CN, >C=O, -CHO, -COOH, -COOR, CH_2=CH-CHO, \text{ etc.}$
- **Hyperconjugation** : It involves delocalisation of  $\sigma$  electrons of C–H bond of an alkyl group directly attached to an atom of unsaturated system or to an atom with an unshared *p*-orbital. For an alkyl group attached to an unsaturated system it decreases with decrease in number of  $\alpha$ -hydrogens :
 
$$CH_3 - > CH_3CH_2 - > (CH_3)_2CH - > (CH_3)_3C -$$

## PEEP INTO PREVIOUS YEARS

5. The increasing order of reactivity of the following compounds towards aromatic electrophilic substitution reaction is



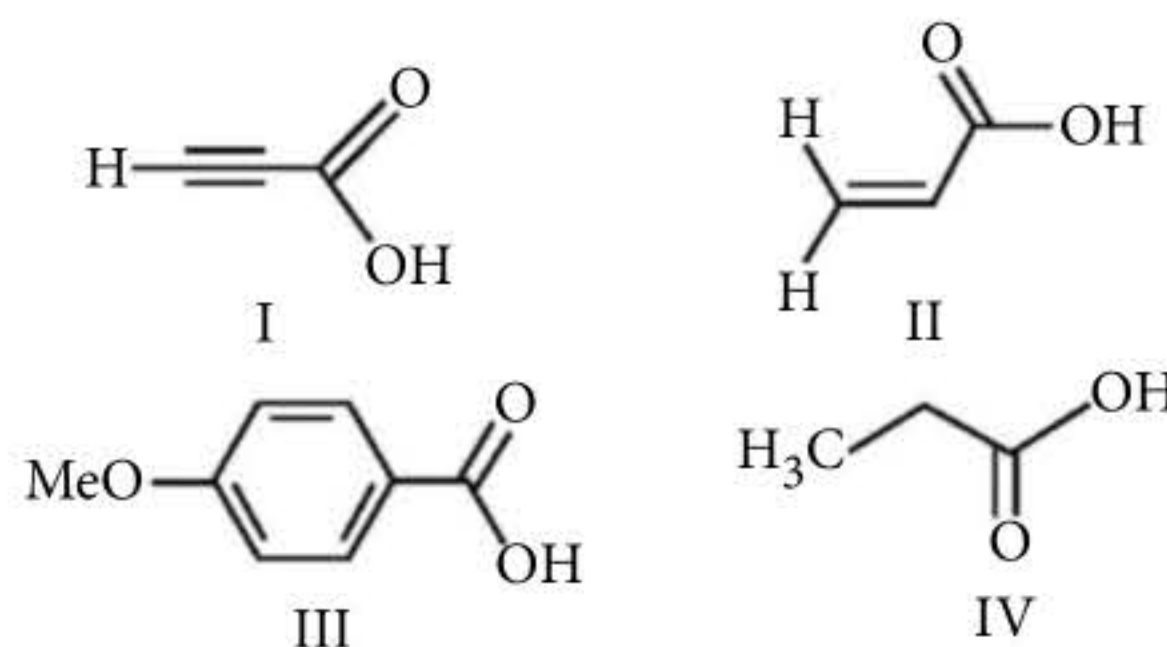
- (a)  $D < B < A < C$       (b)  $B < C < A < D$   
 (c)  $A < B < C < D$       (d)  $D < A < C < B$

(JEE Main 2019)

6. The most stable carbocation, among the following is

- (a)  $(CH_3)_3C-\overset{+}{C}H-CH_3$   
 (b)  $CH_3-CH_2-\overset{+}{C}H-CH_2-CH_3$   
 (c)  $CH_3-\overset{+}{C}H-CH_2-CH_2-CH_3$   
 (d)  $CH_3-CH_2-\overset{+}{C}H_2$       (Odisha NEET 2019)

7. The correct order of acidic strength of the following carboxylic acids is



- (a)  $I > II > III > IV$       (b)  $II > I > IV > III$   
 (c)  $I > III > II > IV$       (d)  $III > II > I > IV$

(JEE Advanced 2019)

8. Which of the following is correct with respect to –*I* effect of the substituents? (*R* = alkyl)

- (a)  $-NH_2 < -OR < -F$   
 (b)  $-NR_2 < -OR < -F$   
 (c)  $-NH_2 > -OR > -F$   
 (d)  $-NR_2 > -OR > -F$

(NEET 2018)

## METHODS OF PURIFICATION OF ORGANIC COMPOUNDS

- Organic compounds can be purified by following methods depending upon the properties of components of mixtures :



Method	Principle	Applications
Crystallisation	Different solubilities of a given organic compound and its impurities in the same solvent.	<ul style="list-style-type: none"> <li>Crystallisation of sugar (containing an impurity of common salt) is achieved by shaking the impure solid with hot ethanol at 348 K (sugar dissolves whereas common salt remains insoluble).</li> </ul>
Sublimation	Some solid substances change from solid to vapour state without passing through liquid state. Sublimable compounds get separated from non-sublimable impurities.	<ul style="list-style-type: none"> <li>Iodine from sodium chloride (as iodine sublimes readily leaving behind sodium chloride).</li> <li>Camphor, naphthalene, anthracene, benzoic acid, etc. are purified.</li> </ul>
Distillation	It is used to separate <ul style="list-style-type: none"> <li>volatile liquids from non-volatile impurities.</li> <li>liquids having sufficient difference in their boiling points.</li> </ul>	<ul style="list-style-type: none"> <li>Hexane (b.p. 342 K) and toluene (b.p. 384 K)</li> <li>Chloroform (b.p. 334 K) and aniline (b.p. 457 K)</li> </ul>
Fractional distillation	If the difference in boiling points of two liquids is not much, this method is used.	<ul style="list-style-type: none"> <li>Crude oil in petroleum industry is separated into various useful fractions such as gasoline, kerosene oil, diesel oil, lubricating oil, etc.</li> </ul>
Distillation under reduced pressure	It is used to purify liquids <ul style="list-style-type: none"> <li>having very high boiling points.</li> <li>which decompose at or below their boiling point.</li> </ul>	<ul style="list-style-type: none"> <li>Glycerol is separated from spent-lye in soap industry.</li> </ul>
Steam distillation	This method is used to separate substances which are steam volatile, immiscible with water, possess a vapour pressure of 10–15 mm Hg and contain non-volatile impurities.	<ul style="list-style-type: none"> <li>Aniline is separated from aniline-water mixture.</li> <li>Essential oils, turpentine oil, <i>o</i>-&amp;<i>p</i>-nitrophenol, bromobenzene, nitrobenzene, etc. can be purified.</li> </ul>
Differential extraction	By shaking an aqueous solution of an organic compound with an organic solvent in which the organic compound is more soluble than in water. The organic solvent and the aqueous solution should be immiscible with each other so that they can form two distinct layers which can be separated by using separating funnel.	<ul style="list-style-type: none"> <li>Benzoic acid can be extracted from its water solution using benzene.</li> </ul>
Chromatography	Differential movement of individual components of a mixture through a stationary phase under the influence of a mobile phase.	<ul style="list-style-type: none"> <li>Widely used for separation, purification, identification and characterisation of the components of a mixture, whether coloured or colourless.</li> </ul>

Types of chromatography	Mobile/Stationary phase
Column chromatography	Liquid/Solid
Thin layer chromatography (TLC)	Liquid/Solid
High performance liquid chromatography (HPLC)	Liquid/Solid

Gas-liquid chromatography (GLC)	Gas/Liquid
Partition or paper chromatography	Liquid/Liquid

- Retention factor ( $R_f$ )  

$$= \frac{\text{Distance travelled by the compound from base line}}{\text{Distance travelled by the solvent from base line}}$$



## QUALITATIVE ANALYSIS OF ORGANIC COMPOUNDS

- In addition to carbon and hydrogen, organic compounds may also contain oxygen, nitrogen, sulphur, halogens and phosphorus. The qualitative analysis of organic compounds involves the detection of all these major elements present in it with the help of suitable chemical tests :

Element	Detection	Confirmatory test	Reactions
Carbon	Copper(II) oxide test $2\text{CuO} + \text{C} \xrightarrow{\Delta} 2\text{Cu} + \text{CO}_2\uparrow$	$\text{CO}_2$ gas turns lime water milky.	$\text{CO}_2\uparrow + \text{Ca(OH)}_2 \xrightarrow{\text{Lime water}} \text{CaCO}_3\downarrow + \text{H}_2\text{O}$ Milkiness
Hydrogen	$\text{CuO} + 2\text{H} \xrightarrow{\Delta} \text{Cu} + \text{H}_2\text{O}$	Water droplets appear on the cooler part of the ignition tube and also turns anhydrous $\text{CuSO}_4$ blue.	$\text{CuSO}_4 + 5\text{H}_2\text{O} \xrightarrow{\text{White}} \text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ Blue
Nitrogen	Lassaigne's extract (L.E.) $\text{Na} + \text{C} + \text{N} \xrightarrow{\Delta} \text{NaCN}$ (L.E.)	L.E. + $\text{FeSO}_4$ + $\text{NaOH}$ , boil and cool + $\text{FeCl}_3$ + conc. $\text{HCl}$ Gives blue or green colour.	$\text{FeSO}_4 + 2\text{NaOH} \xrightarrow{\text{Fe(OH)}_2} \text{Fe(OH)}_2 + \text{Na}_2\text{SO}_4$ $\text{Fe(OH)}_2 + 6\text{NaCN} \xrightarrow{\text{Na}_4[\text{Fe(CN)}_6] + 2\text{NaOH}}$ $3\text{Na}_4[\text{Fe(CN)}_6] + 4\text{FeCl}_3 \xrightarrow{\text{HCl}} \text{Fe}_4[\text{Fe(CN)}_6]_3 + 12\text{NaCl}$ Prussian blue
Sulphur	$2\text{Na} + \text{S} \xrightarrow{\Delta} \text{Na}_2\text{S}$ (L.E.)	<ul style="list-style-type: none"> <li>L.E. + sodium nitroprusside Gives deep violet colour.</li> <li>L.E. + <math>\text{CH}_3\text{COOH}</math> + <math>(\text{CH}_3\text{COO})_2\text{Pb}</math> Gives black ppt.</li> </ul>	$\text{Na}_2\text{S} + \text{Na}_2[\text{Fe(CN)}_5\text{NO}] \xrightarrow{\text{Sodium nitroprusside}} \text{Na}_4[\text{Fe(CN)}_5\text{NOS}]$ Deep violet $\text{Na}_2\text{S} + (\text{CH}_3\text{COO})_2\text{Pb} \xrightarrow{\text{CH}_3\text{COOH}} \text{PbS}\downarrow + 2\text{CH}_3\text{COONa}$ Black ppt.
Halogens	$\text{Na} + \text{X} \xrightarrow{\Delta} \text{NaX}$ (L.E.)	L.E. + $\text{HNO}_3$ + $\text{AgNO}_3$ <ul style="list-style-type: none"> <li>White ppt. soluble in aq. <math>\text{NH}_3</math> (or <math>\text{NH}_4\text{OH}</math>) confirms Cl.</li> <li>Yellow ppt. partially soluble in aq. <math>\text{NH}_3</math> (or <math>\text{NH}_4\text{OH}</math>) confirms Br.</li> <li>Yellow ppt. insoluble in aq. <math>\text{NH}_3</math> (or <math>\text{NH}_4\text{OH}</math>) confirms I.</li> </ul>	$\text{NaX} + \text{AgNO}_3 \xrightarrow{\text{HNO}_3} \text{AgX}\downarrow + \text{NaNO}_3$ ppt. $\text{AgCl} + 2\text{NH}_3(aq) \xrightarrow{\text{White ppt.}} [\text{Ag(NH}_3)_2]\text{Cl}$ Soluble $+ 2\text{H}_2\text{O}$
Nitrogen and sulphur together	$\text{Na} + \text{C} + \text{N} + \text{S} \xrightarrow{\Delta} \text{NaSCN}$ 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.	$\text{NaSCN} + \text{FeCl}_3 \xrightarrow{\text{Fe(SCN)}_3} \text{Fe(SCN)}_3 + 3\text{NaCl}$ Blood red colour
Phosphorus	$\text{P} \xrightarrow[\Delta]{\text{Na}_2\text{O}_2, \text{boil}} \text{Na}_3\text{PO}_4$	Solution is boiled with nitric acid and then treated with ammonium molybdate, $(\text{NH}_4)_2\text{MoO}_4$ . Formation of yellow ppt. indicates presence of phosphate (hence, phosphorus) in organic compound.	$\text{Na}_3\text{PO}_4 + 3\text{HNO}_3 \xrightarrow{\text{H}_3\text{PO}_4 + 3\text{NaNO}_3}$ $\text{H}_3\text{PO}_4 + 12(\text{NH}_4)_2\text{MoO}_4 + 21\text{HNO}_3 \xrightarrow{\text{(NH}_4)_3\text{PO}_4 \cdot 12\text{MoO}_3}$ Ammonium phosphomolybdate (yellow ppt.) $+ 21\text{NH}_4\text{NO}_3 + 12\text{H}_2\text{O}$



## QUANTITATIVE ANALYSIS OF ORGANIC COMPOUNDS

- The percentage composition of elements present in an organic compound is determined by the following methods :

Element	Method
Carbon and Hydrogen	<b>Liebig's Combustion method :</b> $\% \text{ of C} = \frac{12}{44} \times \frac{\text{mass of CO}_2 \text{ formed}}{\text{mass of compound taken}} \times 100; \quad \% \text{ of H} = \frac{2}{18} \times \frac{\text{mass of H}_2\text{O formed}}{\text{mass of compound taken}} \times 100$
Nitrogen	<b>Dumas method :</b> $\% \text{ of N} = \frac{28}{22400} \times \frac{\text{vol. of N}_2 \text{ at STP}}{\text{mass of compound taken}} \times 100$ <b>Kjeldahl's method :</b> $\% \text{ of N} = \frac{1.4 \times \text{molarity of acid} \times \text{vol. of acid used} \times \text{basicity of acid}}{\text{mass of compound taken}}$
Halogens	<b>Carius method :</b> $\% \text{ of X} = \frac{\text{At. mass of X}}{108 + \text{At. mass of X}} \times \frac{\text{mass of AgX formed}}{\text{mass of compound taken}} \times 100$
Sulphur	<b>Carius method :</b> $\% \text{ of S} = \frac{32}{233} \times \frac{\text{mass of BaSO}_4 \text{ formed}}{\text{mass of compound taken}} \times 100$
Phosphorus	<b>Ignition method :</b> $\% \text{ of P} = \frac{62}{222} \times \frac{\text{mass of Mg}_2\text{P}_2\text{O}_7 \text{ formed}}{\text{mass of compound taken}} \times 100$
Oxygen	<b>Iodine method :</b> $\% \text{ of O} = \frac{16}{44} \times \frac{\text{mass of CO}_2 \text{ formed}}{\text{mass of compound taken}} \times 100 \quad \text{or} \quad \% \text{ of O} = \frac{5 \times 16}{2 \times 127} \times \frac{\text{mass of I}_2 \text{ formed}}{\text{mass of compound taken}} \times 100$

### PEEP INTO PREVIOUS YEARS

9. The correct match between items I and II is

Item-I (Mixture)	Item-II (Separation method)
(A) H <sub>2</sub> O : Sugar	(P) Sublimation
(B) H <sub>2</sub> O : Aniline	(Q) Recrystallization
(C) H <sub>2</sub> O : Toluene	(R) Steam distillation
	(S) Differential extraction

- (a) (A) → (Q); (B) → (R); (C) → (S)  
 (b) (A) → (R); (B) → (P); (C) → (S)  
 (c) (A) → (Q); (B) → (R); (C) → (P)  
 (d) (A) → (S); (B) → (R); (C) → (P)

(JEE Main 2019)

10. Two compounds I and II are eluted by column chromatography (adsorption of I > II). Which one of the following is a correct statement?

- (a) II moves faster and has higher  $R_f$  value than I.  
 (b) I moves faster and has higher  $R_f$  value than II.  
 (c) II moves slower and has higher  $R_f$  value than I.  
 (d) I moves slower and has higher  $R_f$  value than II.

(JEE Main Online 2018)

11. The most suitable method of separation of 1 : 1 mixture of *ortho* and *para*-nitrophenols is  
 (a) chromatography (b) crystallisation  
 (c) steam distillation (d) sublimation.

(NEET 2017)

### POINTS FOR EXTRA SCORING

- The problems on structural isomerism and structure determination of organic molecules can be easily solved by the concept of double bond equivalents (D.B.E.) which implies the sum of double bonds and rings present in the molecule.