

# NEET/JEE 2019

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## UNIT - 7 : 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.

|           |                 |                 |                 |
|-----------|-----------------|-----------------|-----------------|
| Structure | Tetrahedral     | Trigonal planar | Linear          |
| Examples  | Ethane, methane | Ethene, propene | Ethyne, propyne |

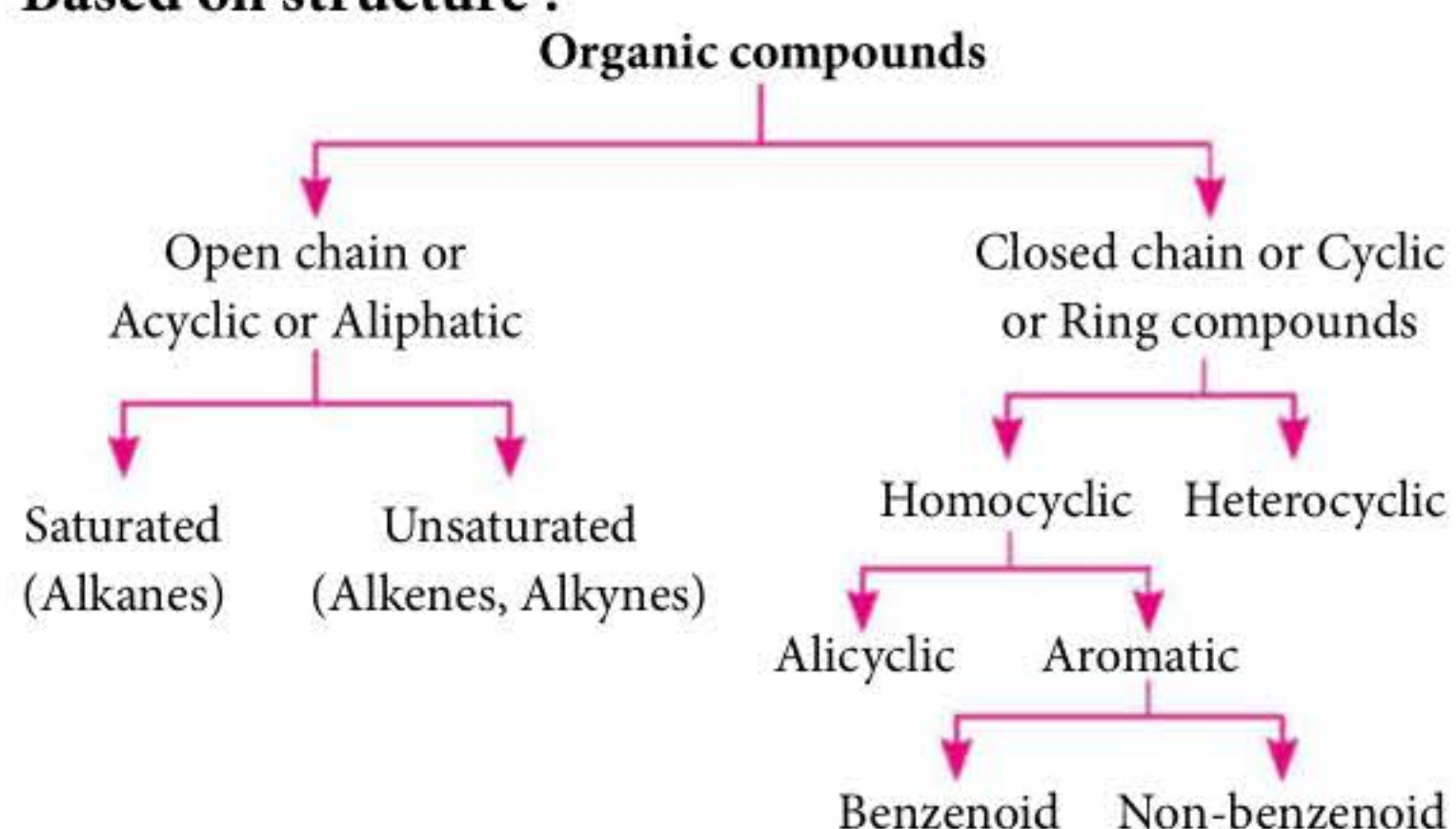
### TETRAVALENCY OF CARBON

Carbon atom has four half filled orbitals in its excited state and hence, forms four covalent bonds.

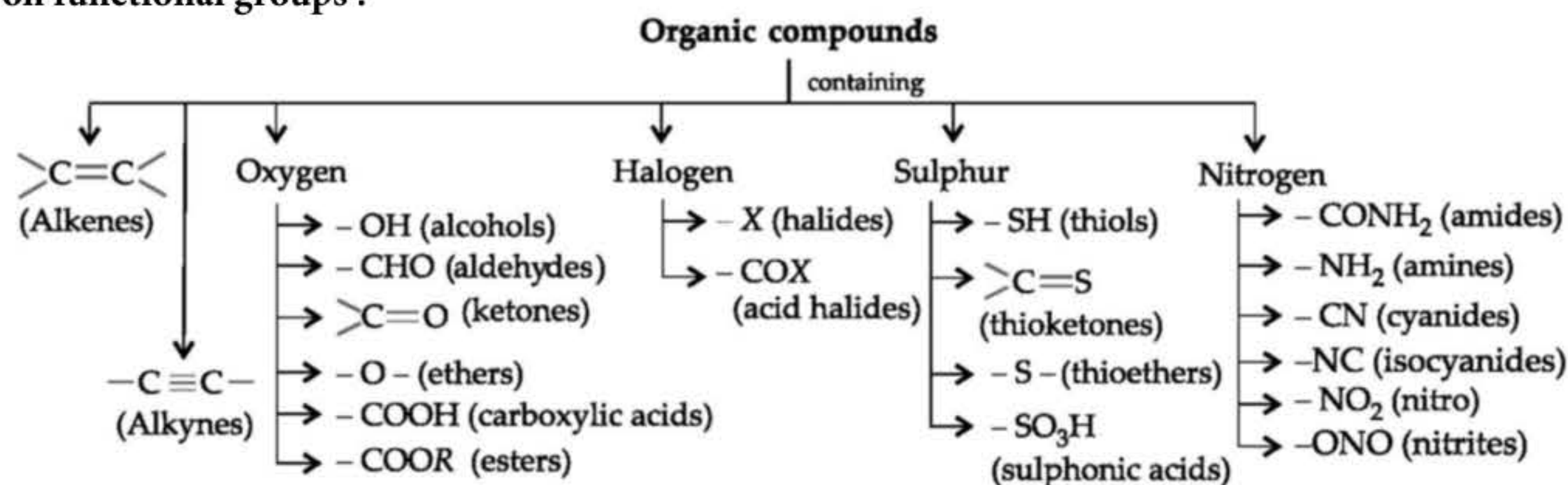
|                                      |        |        |      |
|--------------------------------------|--------|--------|------|
| Hybridisation                        | $sp^3$ | $sp^2$ | $sp$ |
| Number of equivalent orbitals formed | 4      | 3      | 2    |
| Unhybridised orbitals                | 0      | 1      | 2    |

### CLASSIFICATION OF ORGANIC COMPOUNDS

Based on structure :



Based on functional groups :



## NOMENCLATURE OF ORGANIC COMPOUNDS

IUPAC Nomenclature : The complete IUPAC name of an organic compound consists of five parts :

| Secondary prefix  | Primary prefix   | Word root   | Primary suffix   | Secondary suffix                          |
|---|--|---|--|---|
| Indicates the nature of side chains and substituents attached to longest chain selected | Indicates the presence of alicyclic system (cyclo = alicyclic) | Indicates the number of carbon atoms in a suitably selected longest continuous chain of carbon atoms. | Indicates the nature of C—C bond in the longest chain selected<br>(-ane : C—C single bond)<br>(-ene : C=C double bond)<br>(-yne : C≡C triple bond) | Indicates the nature of functional group. |

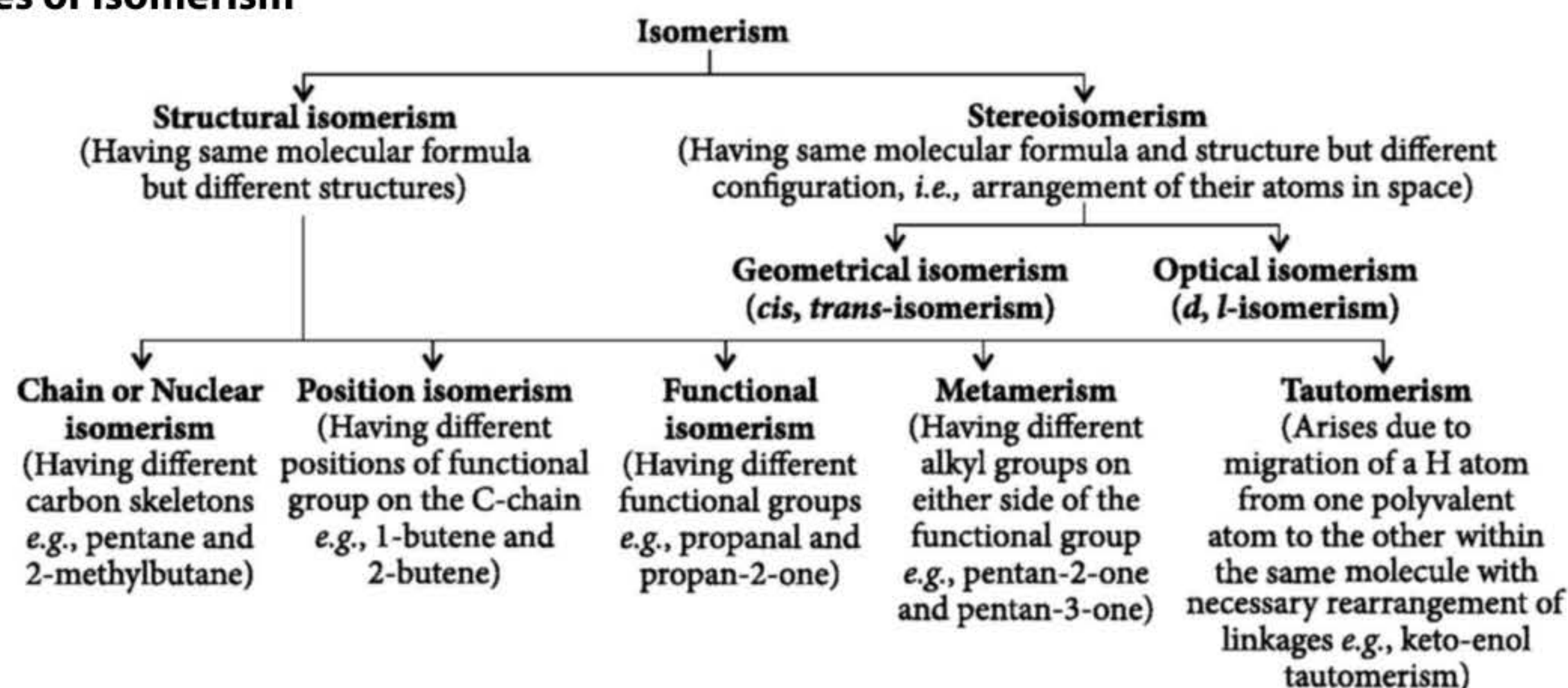
### Rules for Nomenclature

- **Longest chain rule** : The very first step for naming an organic compound is to select longest continuous carbon chain, which may be either straight or branched. This is called principal chain or parent chain.
- **Numbering of the principal chain** : The principal carbon chain is numbered from one end to other by numerals (1, 2, 3, 4, ..... ) in such a way that it gives the lowest possible number to the carbon atom carrying the substituent.
- **Lowest set of locants rule** : When the parent chain has two or more substituents, numbering should be done in such a way that sum of the locants on the parent chain is lowest possible number. This is also known as lowest sum rule.
- **Alphabetical order of the substituents** : When two or more substituents are present on the parent chain, then these substituents prefixed with their position number are arranged in alphabetical order (irrespective of the position number) before word root.
- **Naming same group at different positions** : When the same substituent occurs more than once on the parent chain, position of each substituent separated by commas is mentioned with suitable prefix such as *di* (for two), *tri* (for three), *tetra* (for four).
- **Naming of complex substituent** : If the substituent on the parent chain is complex (*i.e.* branched), it is named as a substituted alkyl group by numbering the group in the same manner as the numbering of parent chain has been done, starting with the carbon atom directly attached to the parent chain.

### ISOMERISM

Two or more compounds possessing same molecular formula but different physical and chemical properties are known as isomers and the phenomenon is called isomerism.

### Types of Isomerism



## REACTION MECHANISM AND INTERMEDIATES

### Fission of a Covalent Bond

- A covalent bond can get cleaved either by :
  - **Heterolytic cleavage** : It involves breaking of a covalent bond in such a fashion that the shared pair of electrons remains with one of

the fragments, which results in the formation of carbocations or carbanions as intermediates.

- **Homolytic cleavage** : It involves breaking of a covalent bond in such a fashion that one of the electrons of the shared pair goes with each of the bonded atom, which results in the formation of free radicals as intermediates.

### 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. | $3^\circ > 2^\circ > 1^\circ$ |

### Attacking Reagents

| Reagent  | Description  | Examples  |
|--|--|---|
| Electrophiles<br>( <i>Electro</i> = Electron, <i>phile</i> = loving) | They are positively charged or neutral molecules having electron deficient atom, seeking a site of high electron density. Electrophiles have an incomplete outer shell and are also called <i>Lewis acids</i> (electron-pair acceptors). | Charged : $H_3O^+$ , $X^+$ (where $X = Cl, Br, I$ ), $NO_2^+$ , $NO^+$ , $NH_4^+$ , $SO_3H^+$ , $C_6H_5N_2^+$ , $R^+$ , $RCO^+$ .<br>Neutral : $BF_3$ , $AlCl_3$ , $FeCl_3$ , $SiCl_4$ , $BeCl_2$ , $ZnCl_2$ , $SO_3$ , $CO_2$ , $CS_2$ , $CX_4$ , $RCOCl$ , $>C=O$ , $\cdot CCl_2$ etc.            |
| Nucleophiles<br>(Nucleo = nucleus, phile = loving)                   | They are negatively charged or neutral molecules having electron-rich atom with unshared electron pair, seeking electron deficient site to attack. They are also called <i>Lewis bases</i> (electron-pair donors).                       | Charged : $H^-$ , $OH^-$ , $X^-$ , $CN^-$ , $N_3^-$ , $RO^-$ , $R^-$ , $RS^-$ , $SH^-$ , $HSO_3^-$ , $NO_2^-$ , $NH_2^-$ , $RCOO^-$ , $HC\equiv C^-$ .<br>Neutral : $\ddot{N}H_3$ , $H_2\ddot{O}$ , $R\ddot{O}H$ , $R\ddot{O}R$ , $R\ddot{S}H$ , $RMgX$ , $Ph_3\ddot{P}$ , $RLi$ , $LiAlH_4$ , etc. |
| Ambiphiles (ambidents)   | They behave like both electrophiles and nucleophiles hence, have dual nature (amphoteric).   | Charged : $H_3\ddot{O}^+$<br>Neutral : $R\ddot{O}H$ , $H\ddot{O}H$ and $R\ddot{P}H_2$ , etc.  |

## ELECTRONIC DISPLACEMENT EFFECTS IN COVALENT BONDS

### Inductive Effect

- It involves 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** :  $-NO_2 > -CN > -COOH > -F > -Cl > -Br > -I > -H$
- Decreasing order of +I effect** :  $(CH_3)_3C^- > (CH_3)_2CH^- > CH_3CH_2^- > CH_3^- > D^- > H^-$

### Electromeric 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** :  $-\text{OH}$ ,  $-\text{OR}$ ,  $-\text{SH}$ ,  $-\text{SR}$ ,  $-\text{NH}_2$ ,  $-\text{NHR}$ ,  $-\text{NR}_2$ ,  $-\text{Cl}$ ,  $-\text{Br}$ ,  $-\text{I}$ , etc.
- **-R or -M effect** :  $>\text{C}=\text{O}$ ,  $-\text{CHO}$ ,  $-\text{COOR}$ ,  $-\text{CN}$ ,  $-\text{NO}_2$ , 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 unsaturated system it decreases with decrease in number of  $\alpha$ -hydrogens :  
 $\text{CH}_3- > \text{CH}_3\text{CH}_2- > (\text{CH}_3)_2\text{CH}- > (\text{CH}_3)_3\text{C}-$

## TYPES OF ORGANIC REACTIONS

### Substitution or Displacement Reactions

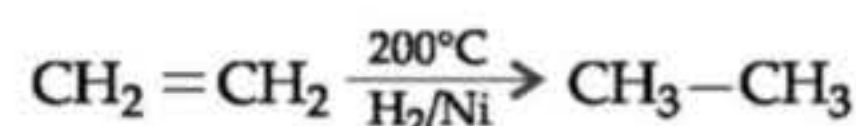
- In these reactions an atom attached to a carbon atom in a molecule is replaced by another atom or group.  
 $\text{CH}_4 + \text{Cl}_2 \xrightarrow{\text{UV light}} \text{CH}_3\text{Cl} + \text{HCl}$
- These are of three types :
  - **Free radical substitution** : When the attacking species is free radical.
  - **Electrophilic substitution** : When the attacking species is electrophile.
  - **Nucleophilic substitution** : When the attacking species is nucleophile.

### Addition Reactions

- In these reactions attacking reagent adds up to the substrate without eliminations.

The methods commonly used for purification are :

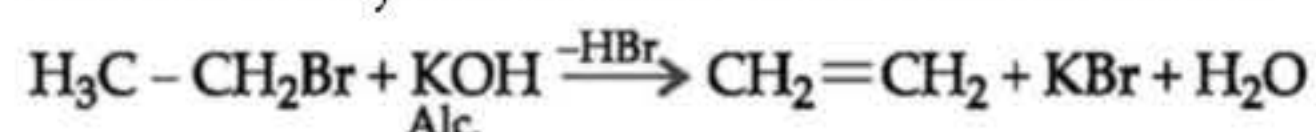
| Method                  | Used for separating   | Examples  |
|-------------------------|---|---|
| Crystallisation         | Mixtures with difference in the solubility of the organic compound and its impurities in a solvent. | • Sugar with impurity of common salt can be crystallised from hot ethanol (sugar dissolves but salt does not).  |
| Sublimation             | Mixtures of sublimable volatile compounds and non-sublimable impurities.                            | • Purification of camphor, anthracene, naphthalene, benzoic acid, etc.  |
| Distillation            | Mixtures of liquids which boil without decomposition and contains non-volatile impurities.          | • Chloroform (b.pt. 334 K) and aniline (b.pt. 457 K).<br>• Ether (b.pt. 308 K) and toluene (b.pt. 383 K).       |
| Fractional distillation | Mixtures of two or more miscible liquids which have b.pt. close to each other.                      | • Acetone (b.pt. 330 K) and methyl alcohol (b.pt. 338 K).<br>• Benzene (b.pt. 353 K) and toluene (b.pt. 384 K). |



- These are also of three types :
  - Free radical addition
  - Electrophilic addition
  - Nucleophilic addition

### Elimination Reactions

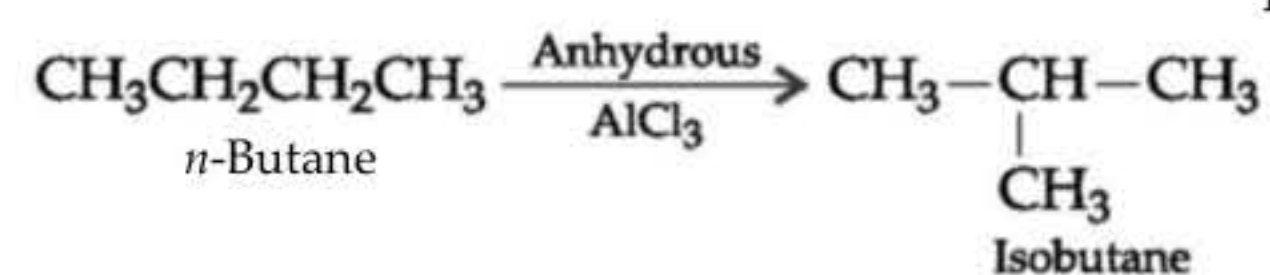
- In these reactions generally atoms from two adjacent atoms are removed and multiple bond is formed. It is just reverse of addition reactions.



- These are of three types:
  - **$\alpha$ -elimination reactions**: Elimination occurs from the same atom of the substrate molecule.
  - **$\beta$ -elimination reactions**: Elimination occurs from the adjacent atom of the substrate molecule.
  - **$\gamma$ -elimination reactions**: Elimination occurs from  $\alpha$ - and  $\gamma$ -positions (*i.e.*, three bonds away) of the substrate molecule leading to the formation of the three-membered rings.

### Rearrangement Reactions

- In these reactions, migration of an atom or a group from one site to another within the molecule takes place.



## METHODS OF PURIFICATION OF ORGANIC COMPOUNDS

- The methods employed for purification depend upon the nature of substance and the type of impurity present in it.

|  |  |   |
|--|--|---|
| 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, (iv) contain non-volatile impurities. | <ul style="list-style-type: none"> <li>Purification of aniline (b.pt. 457 K).</li> <li>Purification of nitrobenzene (b.pt 484 K), etc.</li> </ul>                             |
| Azeotropic distillation                                    | Mixtures with constant boiling points- Azeotropic mixtures.  | <ul style="list-style-type: none"> <li>Ethanol and water in ratio 95.63 : 4.37.</li> </ul>  |
| Distillation under reduced pressure or Vacuum distillation | Mixtures of high boiling liquids which decompose at or below their boiling points.   | <ul style="list-style-type: none"> <li>Glycerol from spent-lye in soap industry (at 453 K under 12 mm Hg).</li> <li>Concentration of sugarcane in sugar industry.</li> </ul>  |
| Chromatography   | Mixtures with difference in the rates at which the components of the mixture move through a stationary phase under the influence of a mobile phase.                                  | <ul style="list-style-type: none"> <li><i>ortho</i> and <i>para</i> nitroanilines.</li> <li>Blue and red dyes.</li> <li>Plant pigments and other natural products.</li> </ul> |
| 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.                             | <ul style="list-style-type: none"> <li>Benzoic acid can be extracted from its water solution using benzene.</li> </ul>  |

## 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<br>$2\text{CuO} + \text{C} \xrightarrow{\Delta} 2\text{Cu} + \text{CO}_2\uparrow$    | $\text{CO}_2$ gas turns lime water milky.  | $\text{CO}_2\uparrow + \text{Ca(OH)}_2 \longrightarrow \text{CaCO}_3\downarrow + \text{H}_2\text{O}$<br>Lime water                      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.   | $\text{CuSO}_4 + 5\text{H}_2\text{O} \longrightarrow \text{CuSO}_4 \cdot 5\text{H}_2\text{O}$<br>White                                      Blue   |
| Nitrogen | Lassaigne's extract (L.E.)<br>$\text{Na} + \text{C} + \text{N} \xrightarrow{\Delta} \text{NaCN}$<br>(L.E.) | L.E. + $\text{FeSO}_4$ + $\text{NaOH}$ , boil and cool + $\text{FeCl}_3$ + conc. $\text{HCl}$<br>Gives blue or green colour.   | $\text{FeSO}_4 + 2\text{NaOH} \longrightarrow \text{Fe(OH)}_2 + \text{Na}_2\text{SO}_4$<br>$\text{Fe(OH)}_2 + 6\text{NaCN} \longrightarrow$<br>$\text{Na}_4[\text{Fe(CN)}_6] + 2\text{NaOH}$<br>$3\text{Na}_4[\text{Fe(CN)}_6] + 4\text{FeCl}_3 \xrightarrow{\text{HCl}}$<br>$\text{Fe}_4[\text{Fe(CN)}_6]_3 + 12\text{NaCl}$<br>Prussian blue |
| Sulphur  | $2\text{Na} + \text{S} \xrightarrow{\Delta} \text{Na}_2\text{S}$<br>(L.E.)                                 | <ul style="list-style-type: none"> <li>L.E. + sodium nitroprusside. A deep violet colour.</li> <li>L.E. + <math>\text{CH}_3\text{COOH}</math> + <math>(\text{CH}_3\text{COO})_2\text{Pb}</math><br/>               Gives a black ppt.</li> </ul> | $\text{Na}_2\text{S} + \text{Na}_2[\text{Fe(CN)}_5\text{NO}] \longrightarrow$<br>Sodium nitroprusside<br>$\text{Na}_4[\text{Fe(CN)}_5\text{NOS}]$<br>Deep violet<br>$\text{Na}_2\text{S} + (\text{CH}_3\text{COO})_2\text{Pb} \xrightarrow{\text{CH}_3\text{COOH}}$<br>$\text{PbS}\downarrow + 2\text{CH}_3\text{COONa}$<br>Black ppt.         |

|                               |   |   |   |
|-------------------------------|---|---|---|
| Halogens                      | $\text{Na} + \text{X} \xrightarrow{\Delta} \text{NaX}$<br>(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> | $\text{NaX} + \text{AgNO}_3 \xrightarrow{\text{HNO}_3} \text{AgX} \downarrow$<br>ppt.<br>$\text{AgCl} + 2\text{NH}_3(\text{aq.}) \longrightarrow [\text{Ag}(\text{NH}_3)_2]\text{Cl}$<br>White ppt. Soluble   |
| Nitrogen and sulphur together | $\text{Na} + \text{C} + \text{N} + \text{S} \xrightarrow{\Delta} \text{NaSCN}$<br>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.  | $3\text{NaSCN} + \text{FeCl}_3 \longrightarrow \text{Fe}(\text{SCN})_3$<br>Blood red colour<br>+ $3\text{NaCl}$   |
| 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.  | $\text{Na}_3\text{PO}_4 + 3\text{HNO}_3 \longrightarrow \text{H}_3\text{PO}_4 + 3\text{NaNO}_3$<br>$\text{H}_3\text{PO}_4 + 12(\text{NH}_4)_2\text{MoO}_4 + 21\text{HNO}_3$<br>$\longrightarrow (\text{NH}_4)_3\text{PO}_4 \cdot 12\text{MoO}_3 \downarrow$<br>Ammonium phosphomolybdate (yellow ppt.)<br>+ $21\text{NH}_4\text{NO}_3 + 12\text{H}_2\text{O}$ |

## QUANTITATIVE ANALYSIS OF ORGANIC COMPOUNDS

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

| Element             | Method   |
|---------------------|--|
| Carbon and Hydrogen | <b>Liebig's Combustion method :</b><br>$\% \text{ of C} = \frac{12}{44} \times \frac{\text{mass of CO}_2 \text{ formed}}{\text{mass of compound taken}} \times 100$ ; $\% \text{ of H} = \frac{2}{18} \times \frac{\text{mass of H}_2\text{O formed}}{\text{mass of compound taken}} \times 100$   |
| Nitrogen            | <b>Dumas method :</b> $\% \text{ of N} = \frac{28}{22400} \times \frac{\text{vol. of N}_2 \text{ at STP}}{\text{mass of compound taken}} \times 100$<br><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><br>$\% \text{ of X} = \frac{\text{At. mass of X}}{108 + \text{At. mass of X}} \times \frac{\text{mass of AgX formed}}{\text{mass of compound taken}} \times 100$  |
| Sulphur             | <b>Carius method :</b><br>$\% \text{ of S} = \frac{32}{233} \times \frac{\text{mass of BaSO}_4 \text{ formed}}{\text{mass of compound taken}} \times 100$  |
| Phosphorus          | <b>Ignition method :</b><br>$\% \text{ of P} = \frac{62}{222} \times \frac{\text{mass of Mg}_2\text{P}_2\text{O}_7 \text{ formed}}{\text{mass of compound taken}} \times 100$  |
| Oxygen              | <b>Iodine method :</b><br>$\% \text{ of O} = \frac{32}{88} \times \frac{\text{mass of CO}_2 \text{ formed}}{\text{mass of compound taken}} \times 100$ or $\% \text{ of O} = \frac{5 \times 16}{2 \times 127} \times \frac{\text{mass of I}_2 \text{ formed}}{\text{mass of compound taken}} \times 100$                                       |