

CLASS 11 Chemistry Chapter 12 Organic chemistry: Some Basic Principles and Techniques

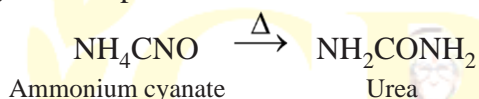
ORGANIC CHEMISTRY

It deals with the study of hydrocarbons (compounds of carbon and hydrogen elements) and their derivatives.

Some organic compounds may also contain nitrogen, oxygen, sulphur, phosphorus, halogens, etc.

Berzelius, proposed that a 'vital force' was responsible for the formation of organic compounds.

This was rejected by F. Wohler who synthesised first organic compound urea from an inorganic compound.



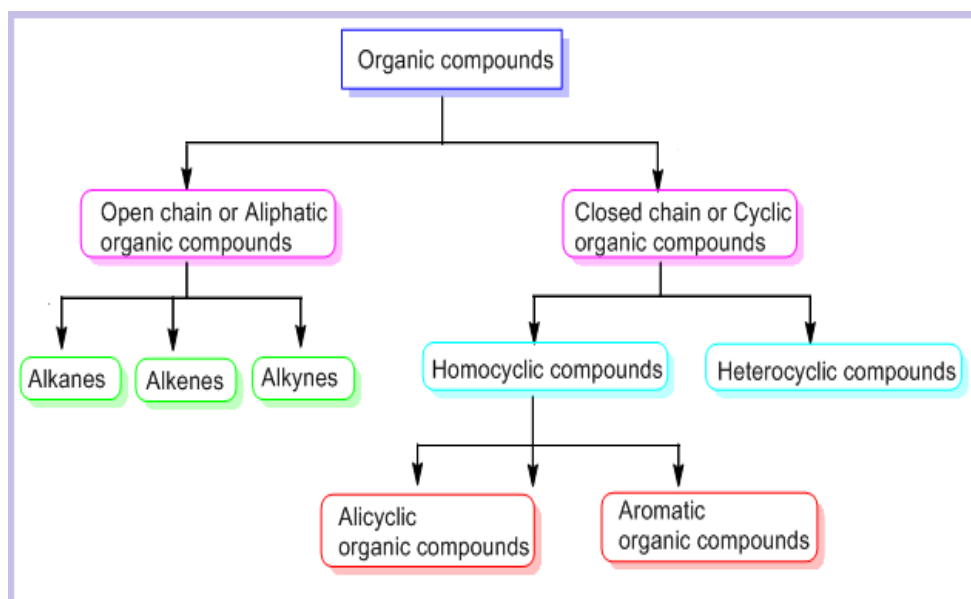
- Acetic acid was synthesized by Kolbe and methane by Berthelot.
- **Types of hybridization of C-atom:**

Hybridization	Structure	Bond angle	Examples
sp^3	Tetrahedral	$109^\circ 28'$	Ethane, Methane
sp^2	Trigonal	120°	Ethene, Propene
sp	Linear	180°	Ethyne, Propyne

- **Reasons for existence of large number of organic compounds:**
- **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.
- **Isomerism:** It is the property by virtue of which two or more compounds have the same molecular formula but different physical or chemical properties.

- **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.

- **CLASSIFICATION OF ORGANIC COMPOUNDS**



- **CLASSIFICATION OF CARBON ATOMS**

On the basis of number of C attached

- (i) **Primary carbon atom:** when carbon atom is attached with one other carbon atom only, it is called **primary or 1°** carbon atom.
- (ii) **Secondary carbon atom:** When carbon atom is attached with two other carbon atoms, it is called **secondary or 2°** carbon atom.
- (iii) **Tertiary carbon atom:** When carbon atom is attached with three other carbon atoms, it is called **tertiary or 3°** carbon atom.
- (iv) **Quaternary carbon atom:** When carbon atom is attached with four

other carbon atoms, it is called **quarterly or 4°** carbon atom.

- **Functional Group:** The atom *e.g.*, -Cl, -Br, etc., or group of atoms *e.g.*, -COOH, -CHO, which is responsible for the chemical properties of the molecule, is called **functional group**.
- **Homologous Series:** The series in which the molecular formula of adjacent members differ by a -CH₂ unit, is called homologous series and the individual members are called homologous, *e.g.*, The homologous series of alkene group is



} difference of -CH₂ unit or 14 unit mass



4 8

The general characteristics of this series are:

1. All the homologues contain same functional group. That's why their chemical properties are almost similar.
2. All the members of a series have same general formula, *e.g.*,

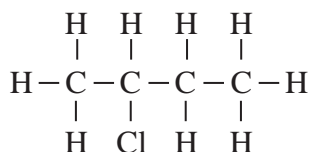
Series	General Formula
Alkanes	C_nH_{2n+2}
Alkenes	C_nH_{2n}
Alkynes	C_nH_{2n-2}
Alcohol and ether	$C_nH_{2n+2}O$
Aldehyde and ketone	$C_nH_{2n}O$
Acid and ester	$C_nH_{2n}O_2$

3. All the members can be prepared by almost similar methods.
4. With increase in the molecular weight of a series, the physical properties vary gradually.

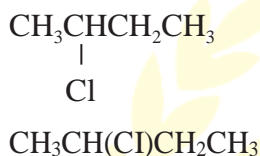
- **Representation of Organic Compounds:**

Organic compounds can be represented by the following ways:

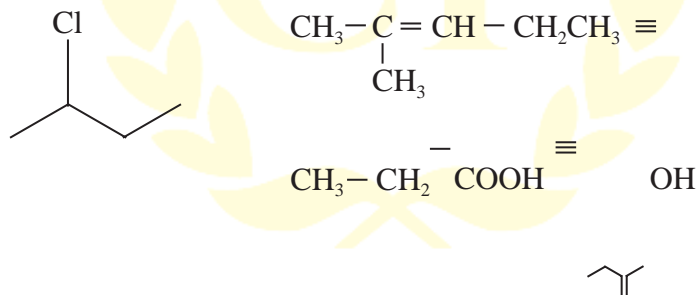
- (i) **Complete Structural Formula:** All the bonds present between any two atoms are shown clearly. *e.g.*,



- **Condensed Formula:** All the bonds are not shown clearly. *e.g.*,



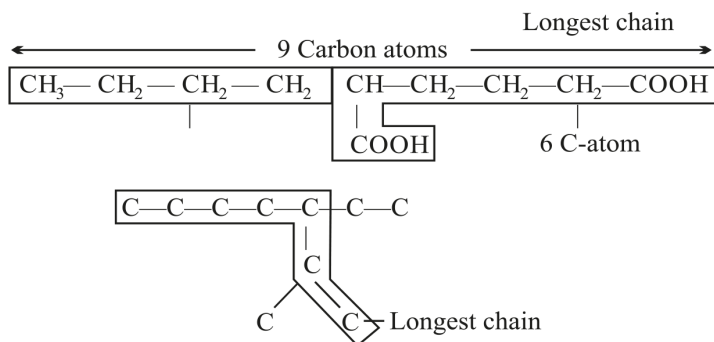
- **Bond Line Formula:** Every fold and free terminal represents a carbon and lines represent the bond. *e.g.*,



- **IUPAC Nomenclature of Organic Compounds:** Following rules are used to write the IUPAC name of an organic compound.

Rule 1.: Longest chain rule: The chain containing the principal functional group, secondary functional group and multiple bonds as many as possible is the longest possible chain.

In the absence of functional group, secondary group and multiple bonds, the chain containing the maximum number of C-atoms will be the longest possible chain *e.g.*,



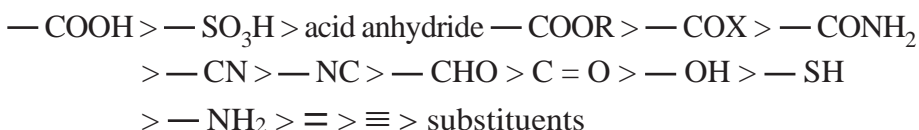
Word Root for Carbon Chain

Chain length	Word root	Chain length	Word root
C ₁	Meth-	C ₇	Hept
C ₂	Eth-	C ₈	Oct
C ₃	Prop-	C ₉	Non
C ₄	But-	C ₁₀	Dec
C ₅	Pent-	C ₁₁	Undec
C ₆	Hex-	C ₁₂	Dodec

Rule 2: Lowest number rule: Numbering is done in such a way so that

- (i) branching if present gets the lowest number.
- (ii) the sum of numbers of side chain is lowest.
- (iii) principal functional-group gets the lowest number.

Select the principal functional group from the preference series :



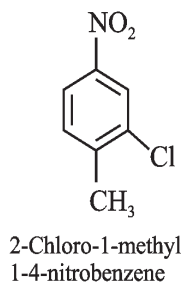
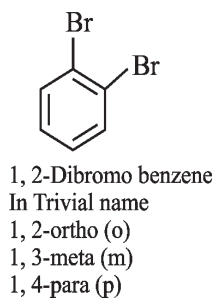
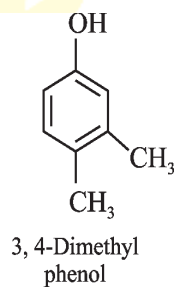
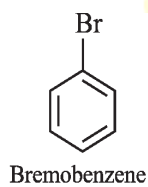
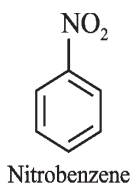
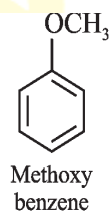
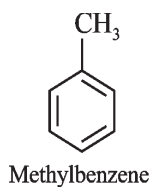
Functional group other than the principal functional group are called substituents.

Rule 3: Naming the prefix and suffixes: Prefix represents the substituent and suffix is used for principal functional group.

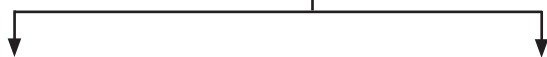
Primary suffix are **ene**, **ane** or **yne** used for double, single and triple bonds respectively.

Secondary suffixes are tabulated below:

No.	Class	Formula	Prefix	Suffix
1.	Acid halides	$\begin{array}{c} \text{O} \\ \\ -\text{C}-\text{X} \end{array}$	halocarbonyl	—oyl halide —carbonyl halide
2.	Alcohols	—OH	hydroxy	—ol
3.	Aldehydes	—CHO	formyl	—al —carbaldehyde
4.	Ketones	C = O	oxo (keto)	—one
5.	Amides	—CONH ₂	carbamoyl	—amide
6.	Amine	—NH ₂	amino	—amine
7.	Carboxylic acid	—COOH	carboxy	—carboxylic acid
8.	Ester	—COOR	alkoxy carbonyl	—alkyl alkanoate
9.	Nitriles	—CN	cyano	—nitrile
10.	Sulphonic acid	—SO ₂ —OH	sulpho	—sulphonic acid



ISOMERISM



Structural isomerism

Same molecular formula but different structures

Types

1. Chain Isomerism

e.g., Pentane and 2-Methylbutane

2.

Position Isomerism

e.g., But-1-ene
But-2-ene

3. Functional Isomerism

e.g., Propanal & Propanone
Ethanol & Methoxymethane

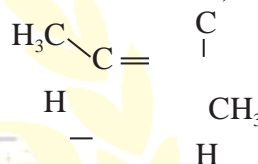
4. Metamerism

e.g., Pentan-2-one and
Pentan-3-one

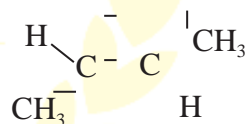
Stereo isomerism

Same molecular and structural formula but different configuration

e.g., Geometrical isomerism
(cis-trans isomerism)



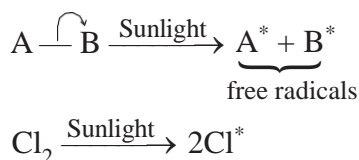
Cis.But-2-ene



Trans.But-2-ene

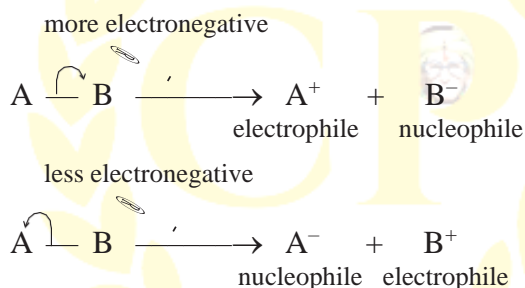
- **Fission of a Covalent Bond:**

- (i) **Homolytic Fission:** In this one of the electrons of the shared pair in a covalent bond goes with each of the bonded atoms. The neutral chemical species thus formed, are called free radicals. Generally, homolytic fission takes place in non-polar covalent molecules in the presence of sunlight or high temperature.



Free radicals are highly reactive, neutral and electron deficient species.

- (ii) **Heterolytic Fission:** The covalent bond breaks in such a fashion that the shared pair of electrons goes with one of the fragments.



Heterolytic fission generally takes place in polar covalent molecules but in non-polar molecules, it takes place in the presence of catalyst like AlCl_3 (anhy.), FeCl_3 (anhy.) etc.

- **Attacking Reagents:**

These are of two types

- (i) **Electrophiles or Electrophilic Reagents**

These are electron deficient species, i.e., behave as Lewis acids.
e.g., Cl^+ , NO_2^+ , CH_3CO^+ etc.

BF_3 , ZnCl_2 (anhydrous), FeCl_3 (anhydrous), AlCl_3 (anhydrous)

- (ii) **Nucleophiles or Nucleophilic Reagents**

These are negatively charged or neutral molecules with unshared

electron pair.

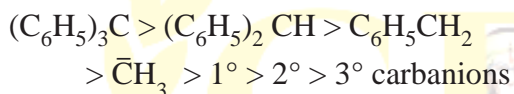


● **Reaction Intermediates:**

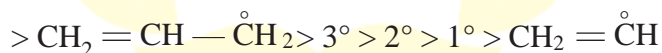
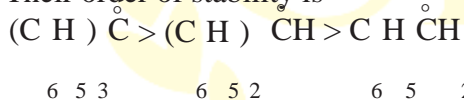
(i) **Free radicals:** These are the product of homolysis and contain an odd electron. These are highly reactive planar species with sp^2 hybridization.

(ii) **Carbanions:** These are the product of heterolysis and contain a carbon bearing negative charge and 8 electrons in its valence shell.

These have pyramidal shape with sp^3 hybridised carbon (having one lone pair) order of stability of carbanions is

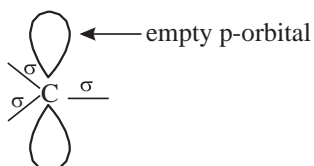


Their order of stability is

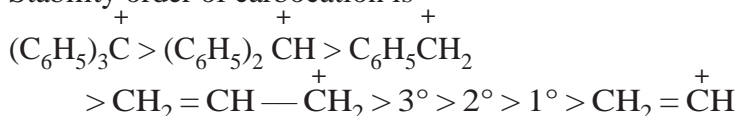


(iii) **Carbocations:** These are the product of heterolysis and contain a carbon bearing positive charge. These are electron deficient species.

These are also polar chemical species i.e., sp^2 hybridised with an empty p-orbital.

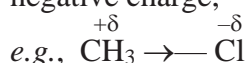


Stability order of carbocation is



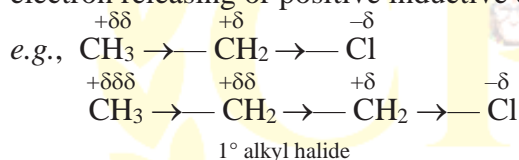
- **Electron Displacement in Covalent Bond**

1. **Inductive Effect:** If shared pair is more shifted towards more electronegative atom, the less electronegative atom acquires slight positive charge and more electronegative atom acquires partial negative charge,

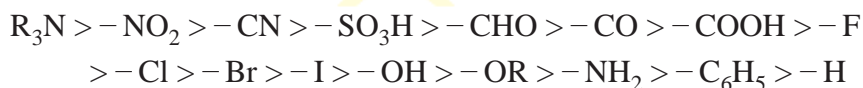


Permanent effect and propagates through carbon chain.

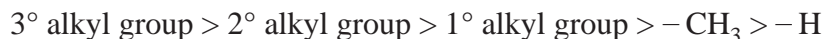
Atoms or groups having greater electron affinity than hydrogen are said to have electron attracting or negative inductive effect ($-I$) while that having, smaller electron affinity than hydrogen are said to have electron releasing or positive inductive effect ($+I$).



Cl has $-I$ effect and alkyl group has $+I$ effect. Order of groups producing $-I$ effect is



Order of groups producing $+I$ effect is

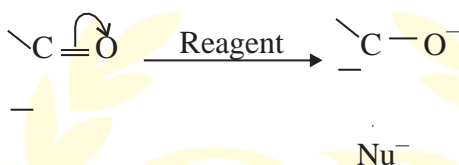
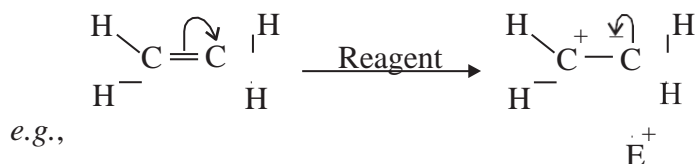


- **Applications of Inductive Effect**

- (i) Presence of groups showing $+I$ effect increases the stability of carbocation while presence of groups showing $-I$ effect decreases their stability.
- (ii) Strength of acid increases with the attachment of group showing $-I$ effect and decreases with the attachment of group showing $+I$ effect.
- (iii) Presence of $+I$ showing groups increases the basic strength of amines.

2. **Electromeric Effect:** Defined as the polarity produced in a multiple bonded compound as a reagent approaches it. In the presence of attacking reagent, the two π electrons are completely transferred to any of the one atom. This effect is temporary.

It may be of +E type (when displacement of electron pair is away from the atom of group) or of -E type (when displacement is towards the atom or group).



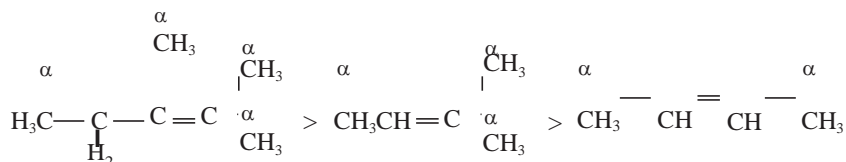
3. **Hyper-conjugation:** It involves delocalization of σ electron of a C - H bond of an alkyl group attached directly to an atom of unsaturated system or to an atom with an unshared p-orbital.



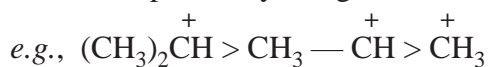
This effect is also called no bond resonance or Baker Nathan effect.

Applications of Hyper-conjugation

Stability of alkenes: More the number of α -hydrogen atoms, more stable is the alkene.



Stability of Carbocation: Greater the number of alkyl groups attached to positively charged carbon atom, the greater is the stability.



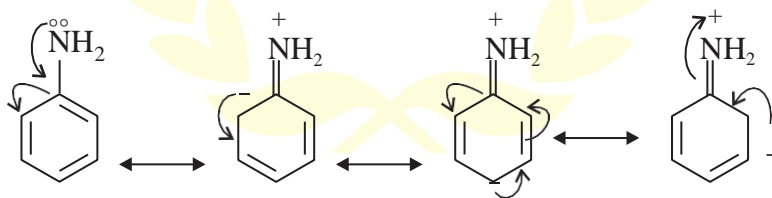
4. **Resonance Effect:** When the properties of a molecule cannot be shown by a single structure and two or more structures are required to show all the properties of that molecule, then the structures are called resonating structures or canonical forms and the molecule is referred as resonance hybrid. This phenomenon is called resonance.

Conditions for resonance

- (i) The arrangement of atoms must be identical in all the formula.
- (ii) The energy content of all the canonical forms must be nearly same.
- (iii) Each canonical of π electrons. This effect may be of +R type or -R type.

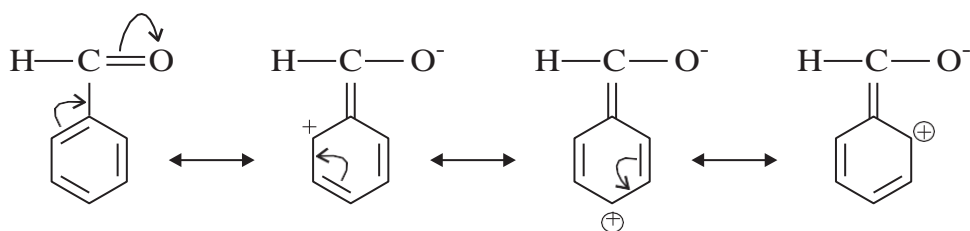
Positive Resonance Effect (+R)

Electron donating groups with respect to conjugated system show +R effect. Central atom of functional groups should be more electronegative than the surrounding atoms or groups to show +R effect. *e.g.*, halogens, -OH, -OR, -NH₂, NHCOR, etc.



Negative Resonance Effect (-R)

Electron withdrawing groups with respect to conjugate system show -R effect. Central atom of functional groups should be less electronegative than surrounding atoms or groups to show -R effect. *e.g.*, halogens, -COOH, -COOR, CHO, -CN, -NO₂, etc.



● **Methods of Purification of Organic Compounds**

Method	Principle	Applications
Crystallization	Different solubilities of a given organic compound and its impurities in the same solvent.	<ul style="list-style-type: none"> Crystallization of sugar (containing an impurity of common salt) is achieved by shaking the impure solid with hot ethanol at 348K (sugar dissolves whereas common salt remains insoluble).
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"> Iodine from sodium chloride (as iodine sublimes readily leaving behind sodium chloride). Camphor, naphthalene, anthracene, benzoic Acid, etc. are purified.
Distillation	It is used to separate <ul style="list-style-type: none"> • Volatile liquids from non-volatile impurities. • Liquids having sufficient difference in their boiling points. 	<ul style="list-style-type: none"> • Hexane (b.p. 342K) and toluene (b.p. 384K) • Chloroform (b.p. 334K) and aniline (b.p. 457K)
– Fractional Distillation	If the difference in boiling points of two liquids is not much, this method is used.	<ul style="list-style-type: none"> • Crude oil in petroleum industry is separated into various useful fractions such as gasoline, kerosene oil, diesel oil, lubricating oil, etc.
– Steam Distillation	This method is used to separate substances which are (i) steam volatile, (ii) immiscible with water, (iii) possess a vapour pressure of 10-15 mm Hg and (iv) contain non-volatile impurities.	<ul style="list-style-type: none"> • Aniline is separated from aniline water mixture. • Essential oils, turpentine oil, o-nitrophenol, bromobenzene nitrobenzene, etc. can be purified.
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"> • Benzoic acid can be extracted from its water solution using benzene.

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"> Widely used for separation purification, identification and characterization of the components of a mixture, whether coloured or colourless.
– Adsorption Chromatography	Differential adsorption of the various components of a mixture on a suitable adsorbent such as silica gel or alumina.	
– Column Chromatography	The mixture is passed through adsorbent packed in glass tube.	<ul style="list-style-type: none"> Mixture of naphthalene and benzophenone.
– Thin Layer Chromatography	The mixture is passed over adsorbent on a thin glass plate.	<ul style="list-style-type: none"> Amino acids can be detected by spraying the plate with ninhydrin solution.
– Partition Chromatography	Differential partitioning of components of a mixture between stationary and mobile phases.	
– Paper Chromatography	A special quality paper known as chromatography paper is used. It contains water trapped in it, which acts as the stationary phase.	<ul style="list-style-type: none"> For separation of sugars and amino acids.

Types of Chromatography	Mobile / Stationary Phase
Column Chromatography	Liquid / Solid
Thin Layer Chromatography	Liquid / Solid
High Performance Liquid Chromatography (HPLC)	Liquid / Solid
Gas Liquid Chromatography (GLC)	Gas / Solid
Partition or Paper Chromatography	Liquid / Solid

Element	Detection	Confirmatory Test	Reactions
Carbon	$2\text{CuO} + \text{C} \xrightarrow{\Delta} 2\text{Cu} + \text{CO}_2$	CO_2 gas turns lime water milky.	$\text{CO}_2 + \text{Ca(OH)}_2 \longrightarrow \text{CaCO}_3 \downarrow + \text{H}_2\text{O}$ 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 CuSO_4 blue.	$\text{CuSO}_4 + 5\text{H}_2\text{O} \longrightarrow \text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ White 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 + $\text{FeCl}_3 + \text{conc. HCl}$. Gives blue or green colour.	$\text{FeSO}_4 + 2\text{NaOH} \longrightarrow \text{Fe(OH)}_2 + \text{Na}_2\text{SO}_4$ $\text{Fe(OH)}_2 + 6\text{NaCN} \longrightarrow$ $\text{Na}_4[\text{Fe(CN)}_6] + 2\text{NaOH}$ $3\text{Na}_4[\text{Fe(CN)}_6] + 4\text{FeCl}_3 \longrightarrow$ $\text{Fe}_4[\text{Fe(CN)}_6]_3 + 12\text{NaCl}$ Prussian blue

Sulphur	$2\text{Na} + \text{S} \xrightarrow{\Delta} \text{Na}_2\text{S}$ (L.E.)	<ul style="list-style-type: none"> - L.E. + sodium nitroprusside A deep violet colour. - L.E. + $\text{CH}_3\text{COOH} + (\text{CH}_3\text{COO})_2\text{Pb}$ Gives a black ppt. 	$\text{Na}_2\text{S} + \text{Na}_2[\text{Fe}(\text{CN})_5\text{NO}] \longrightarrow$ Sodium nitroprusside $\text{Na}_4[\text{Fe}(\text{CN})_5\text{NOS}]$ Deep violet CH_3COOH $\text{Na}_2\text{S} + (\text{CH}_3\text{COO})_2\text{Pb} \longrightarrow$ $\text{PbS} \downarrow + 2\text{CH}_3\text{COONa}$ Black ppt.
Halogens	$\text{Na} + \text{X} \xrightarrow{\Delta} \text{NaX}$ (L.E.)	<ul style="list-style-type: none"> L.E. + $\text{HNO}_3 + \text{AgNO}_3$ - White ppt. soluble in aq. NH_3 (or NH_4OH) confirms Cl. - Yellow ppt. partially soluble in aq. NH_3 (or NH_4OH) confirms Br. - Yellow ppt. insoluble in aq. NH_3 (or NH_4OH) confirms I. 	$\text{NaX} + \text{AgNO}_3 \xrightarrow{\text{HNO}_3} \text{AgX} \downarrow$ ppt. $\text{AgCl} + 2\text{NH}_3(\text{aq.}) \longrightarrow [\text{Ag}(\text{NH}_3)_2]\text{Cl}$ White ppt. Soluble
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.	$\text{NaSCN} + \text{FeCl}_3 \longrightarrow$ $[\text{Fe}(\text{SCN})\text{Cl}_2] + \text{NaCl}$ Blood red colour
Phosphorus	$\text{P} \xrightarrow{\text{Na}_2\text{O}_2, \text{boil}} \text{Na}_3\text{PO}_4$	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.	$\text{Na}_3\text{PO}_4 + 3\text{HNO}_3 \longrightarrow \text{H}_3\text{PO}_4 + 3\text{NaNO}_3$ $\text{H}_3\text{PO}_4 + 12(\text{NH}_4)_2\text{MoO}_4 + 21\text{HNO}_3 \longrightarrow (\text{NH}_4)_3\text{PO}_4 \cdot 12\text{MoO}_3$ 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 methods based on the following principles:

Elements	Method
Carbon and Hydrogen	<p>Liebig's Combustion method: A known mass of an organic compound is burnt in the presence of excess of O₂ and CuO.</p> $\text{C}_x \text{H}_y + \left(x + \frac{y}{4}\right) \text{O}_2 \xrightarrow{\Delta} x \text{CO}_2 + \frac{y}{2} \text{H}_2\text{O}$ <p>CO₂ evolved is absorbed by conc. solution of KOH or ascarite (NaOH + CaO). H₂O produced is absorbed by anhydrous CaCl₂ or Mg(ClO₄)₂. Increase in masses of these absorbing compounds gives the masses of CO₂ and H₂O produced.</p> <p>% of C = $\frac{12}{44} \times \frac{\text{mass of CO}_2 \text{ formed}}{\text{mass of compound taken}} \times 100$;</p> <p>% of H = $\frac{2}{18} \times \frac{\text{mass of H}_2\text{O formed}}{\text{mass of compound taken}} \times 100$</p>
Halogens	<p>Carius method: Halogen in organic compound is precipitated as silver halide by boiling with conc. HNO₃ and then adding AgNO₃.</p> $\text{X} \xrightarrow[\text{AgNO}_3]{\text{HNO}_3, \Delta} \text{AgX} \downarrow$ <p>% of X = $\frac{\text{At. mass of X}}{108 + \text{At. mass of X}} \times \frac{\text{mass of AgX formed}}{\text{mass of compound taken}} \times 100$</p>
Nitrogen	<p>Dumas method: Nitrogen containing organic compound is heated with CuO in an atmosphere of CO₂.</p> $\text{C}_x \text{H}_y \text{N}_z + \left(2x + \frac{y}{2}\right) \text{CO} \longrightarrow x \text{CO}_2 + \frac{y}{2} \text{H}_2\text{O} + \text{N}_2 + \left(2x + \frac{y}{2}\right) \text{Cu}$ <p>N₂ evolved gets collected over conc. KOH solution which absorbs all other gases.</p> <p>% of N = $\frac{28}{22400} \times \frac{\text{Vol. of N}_2 \text{ at STP}}{\text{mass of compound taken}} \times 100$</p> <p>Kjeldahl's method: Organic compound + H₂SO₄ (conc.) \longrightarrow (NH₄)₂SO₄ $\xrightarrow{2\text{NaOH}}$ Na₂SO₄ + 2NH₃ + 2H₂O + 2NH₃ + H₂SO₄ \longrightarrow (Na₄)₂SO₄</p> <p>% of N = $\frac{1.4 \times \text{molarity of acid} \times \text{vol. of acid used} \times \text{basicity of acid}}{\text{mass of compound taken}}$</p>

Sulphur	<p>Carius method: Sulphur in organic compound is converted into H_2SO_4 by boiling with Na_2O_2 or conc. HNO_3 and is precipitated as BaSO_4 by adding excess of BaCl_2 solution in water.</p> $\text{S} \xrightarrow[\text{(ii) BaCl}_2]{\text{(i) HNO}_3, \Delta} \text{BaSO}_4 \downarrow$ <p style="text-align: center;">white ppt.</p> $\% \text{ of S} = \frac{32}{233} \times \frac{\text{mass of BaSO}_4 \text{ formed}}{\text{mass of compound taken}} \times 100$
Phosphorus	<p>Ignition method:</p> $\text{P} \xrightarrow[\text{heat}]{\text{HNO}_3} \text{H}_3\text{PO}_4$ $\text{H}_3\text{PO}_4 + \text{Mg}^{2+} + \text{NH}_4\text{Cl} \xrightarrow{\Delta} \text{MgNH}_4\text{PO}_4 + \text{HCl}$ <p style="text-align: center;">Magnesium ammonium phosphate (white ppt.)</p> $2\text{MgNH}_4\text{PO}_4 \xrightarrow{\Delta} \text{Mg}_2\text{P}_2\text{O}_7 + 2\text{NH}_3 + \text{H}_2\text{O}$ <p style="text-align: center;">Magnesium pyrophosphate</p> $\% \text{ of P} = \frac{62}{222} \times \frac{\text{mass of Mg P}_2\text{O}_7 \text{ formed}}{\text{mass of compound taken}} \times 100$

ORGANIC CHEMISTRY: AT A GLANCE

