Structural Identification & POC

Introduction

The main objective of an organic chemist is the determination of the structure of a new organic compound which has been obtained in pure state either from a natural source or synthesised in the laboratory. In order to establish the correct structure of an organic compound, it is necessary to detect skeleton of compound, elements and functional groups present in the organic compound.

Section (A): Degree of unsaturation and catalytic hydrogenation

1. Hydrogen deficiency index or degree of unsaturation:

The presence of double bonds or rings within a molecule is indicated by a quantity called hydrogen deficiency index.

Applications : To indentify the no. of π bonds or rings and also helpful in determining the structure of the molecule.

Definition: Deficiency of 2H atoms with respect to fully saturated acyclic hydrocarbon is equivalent to One HDI It is also known as Double Bond Equivalence (DBE) or degree of unsaturation (DU).

$$\begin{array}{c} CH_3 - CH = CH_2 \\ Or \\ OU = O) \end{array} \xrightarrow{-2H} \begin{array}{c} CH_3 - CH = CH_2 \\ OI \\ OU = 1) \end{array} \xrightarrow{-2H} CH_3 - C = CH \text{ or } CH_2 = C = CH_2 \text{ or } (DU = 2) \end{array}$$

Degree of unsaturation (D.U.) =
$$\frac{(2n+2)-(No.of \ H \ atoms+No.of \ X \ atoms-No.of \ N \ atoms)}{2}$$

Where n = number of carbon atoms in the molecule

Note: Total no. of cyclic rings + double bonds will give us degree of unsaturation.

One double bond = one DU

One ring = one DU

One triple bond = two DU

Ex. (i)
$$CH_2 = CH_2$$
 $DU = \frac{(2 \times 2 + 2) - 4}{2} = 2/2 = 1$ (ii) $DU = 2$ (iv) $DU = 7$ (v) C_6H_6O $DU = \frac{(2n + 2) - 6}{2} = \frac{14 - 6}{2} = 4$ (vi) C_6H_5CI $D.U. = \frac{14 - (5 + 1)}{2} = 4$

2. Catalytic hydrogenation:

Alkenes, Alkynes, polyenes or polyynes can be hydrogenated by using catalysts Ni/Pt/Pd at room temperature.

All Carbon–Carbon π bonds(C=C, C=C) get hydrogenate. The reaction can't be stopped at any intermediate stage.

Note: (i) Aromatic π bonds are stable at room temperature but can be hydrogenated at high temperature.

- (ii) It can be concluded that the hydrogenation product of an alkene or alkyne or any unsaturated compound is always a saturated compound.
- (iii) The no. of moles of H_2 consumed by 1 mole of compound is equal to the no. of π bonds.
- (iv) During catalytic hydrogenation carbon skelton does not change.

Application : This reaction gives an information about molecule that the molecule is saturated or unsaturated.

General reaction:

(a) R-CH=CH-R + H2
$$\xrightarrow{\text{Ni}}$$
 R-CH2-CH2-R
(b) R-C=C-R + 2H2 $\xrightarrow{\text{Ni/Pt/Pd}}$ R-CH2-CH2-R
 \downarrow^{H_2} R-CH=CH-R
(Not isolated) $\xrightarrow{\text{H}_2}$ R-CH2-CH2-R
(c) CH2=CH-CH=CH2 $\xrightarrow{\text{CH}_2/\text{Ni}}$ CH3-CH2-CH2-CH3
 $\xrightarrow{\text{CH} = \text{CH}_2}$ $\xrightarrow{\text{CH}_2/\text{Ni}}$ room temperature $\xrightarrow{\text{CH}_2 - \text{CH}_3}$
(d) $\xrightarrow{\text{CH}_2/\text{Ni}}$ $\xrightarrow{\text{CH}_2 - \text{CH}_3}$

Section (B): Monochloroination & ozonolysis reactions

3. Monohalogenation:

When an alkane or a cycloalkane is treated with halogen (Cl₂, Br₂, F₂, I₂), a photochemical reaction takes place, in which a C–H bond cleaves and a C–X bond is formed. In such reactions if one H-atom is substituted by one halogen atom, then this is known as monohalogenation reaction.

Applications: If a molecule has more than one type of H-atoms, then on monochlorination, it forms a mixture of monochloroisomers. **All these products (structures) are position isomers.**

Conclusion: Hence, it can be concluded that the total no. of position isomers (structural) of monochloro compounds is equal to the number of different types of H-atoms present in the reactant. The different type of H-atoms are also known as non-identical Hydrogens or non-equivalent Hydrogens or chemically different Hydrogens.

Note: In aromatic hydrocarbons, the hydrogen atoms of the side-chain are chlorinated, but H-atoms of Benzene ring are stable.

½1–Monochloroproduct½

Note: Only one monochloro product is formed because aromatic H atoms are inert towards this reaction.

(iv) CH₃-CH₂-CH₂-CH₃
$$\xrightarrow{\text{Cl}_2, \text{ hv}}$$
 2 Products (structure isomers)
(v) CH₃-CH₂-CH₂-CH₃ $\xrightarrow{\text{Monochlorination}}$ 3 Products (structure isomers)
CH₃ $\xrightarrow{\text{Cl}_2, \text{ hv}}$ $\xrightarrow{\text{Monochlorination}}$ 4 Products (structure isomers)

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4. Ozonolysis:

Ozonolysis reaction is used to determine the position of C=C, C≡C in a molecule. In this reaction Alkene, Alkyne and polyalkene on ozonolysis undergo oxidative cleavage. It is of two types.

(i) Reductive ozonolysis

Reagents are: (1) O₃ (ozone) (2) Zn or (CH₃)₂S and H₂O or CH₃COOH

The products are carbonyl compounds (aldehydes or ketones).

(ii) Oxidative ozonolysis

Reagents are: (1) O₃ (ozone) (2) H₂O₂ or H₂O

The products are ketones and/or acids.

Note: (i) Ozonolysis does not interfere with other functional groups.

(ii) At higher temperature, the aromatic double bonds can also undergo ozonolysis reaction.

General Reaction:

(i) Reductive ozonolysis

(ii) Oxidative ozonolysis

Ex. (a) CH₂=CH₂ (2) Zn/H₂O CH₂=O + CH₂=O
$$\xrightarrow{\text{(1) O}_3}$$

(c) CH2=CH-CH2-CH=CH-CH3
$$^{(2)}$$
 Zn/H2O CH2=O + O=CH-CH2-CH=O + O=CH-CH3

(d)
$$\xrightarrow{(1) O_3}$$
 2OHC-CH2-CHO (Propandial)

(e)
$$\xrightarrow{(1) O_3}$$
 $\xrightarrow{(2) Zn/H_2O}$ O=CH-CH₂-O-CH₂-CH=O + O=CH₂

(f)
$$\xrightarrow{(1) O_3(\Delta)}$$
 $\xrightarrow{(2) H_2O_2}$ $\xrightarrow{(2) H_2O_2}$ $\xrightarrow{(2) H_2O_2}$ $\xrightarrow{(2) H_2O_2}$ $\xrightarrow{(3) O_3(\Delta)}$ $\xrightarrow{(2) H_2O_2}$ $\xrightarrow{(3) O_3(\Delta)}$ $\xrightarrow{(2) H_2O_2}$ $\xrightarrow{(3) O_3(\Delta)}$ $\xrightarrow{(2) H_2O_2}$ $\xrightarrow{(3) O_3(\Delta)}$ $\xrightarrow{(3) O_3(\Delta)}$ $\xrightarrow{(4) O_3(A)}$ $\xrightarrow{(4) O_$

$$(i)O_{3} + CH_{3}CH=O$$

$$(i)O_{3} + CH_{3}CH=O$$

$$(i)O_{3},\Delta$$

$$(i)O_{3},\Delta$$

$$(i)O_{3},\Delta$$

$$(ii)Zn, H_{2}O$$

$$2 O=CH-CH=O + O=CH-C-CH=O + CH_{3}CH=O$$

Practical Organic Chemistry (POC):

When we are looking for the information regarding the functional nature of the compound then we go for the following lab test.

Section (C & D): Test for acidic hydrogen, unsaturation & functional groups

(1) Test for acidic/active hydrogen:

When any compound release H₂ gas after reaction with sodium or potassium or alkali metals or sodamide then this reflects the presence of acidic hydrogen.

Active H: Those H atoms which is attached with more electronegative atoms like O,N,S,X, Csp.

General reaction : $Z - \bigoplus + Na \rightarrow \overline{Z} \stackrel{+}{N}a + \frac{1}{2} H_{2\uparrow}$

Ex. (a)
$$R-NH_2 \xrightarrow{Na} R-NHNa + \frac{1}{2}H_2 \uparrow$$

$$R - COOH \xrightarrow{\text{Na}} R - COONa + \frac{1}{2}H_2 \uparrow$$

(e) R—OH + Na
$$\rightarrow$$
 R—O-Na+ + $\frac{1}{2}$ H₂↑

(a) R—C≡CH + Na → R—C≡C-Na⁺ +
$$\frac{1}{2}$$
 H₂ ↑

(i) R —
$$CH_2$$
— O — CH_3 + $Na \rightarrow No$ reaction.

(k)
$$\stackrel{H}{\longrightarrow}$$
 + Na \rightarrow $\stackrel{\ominus}{\longrightarrow}$ Na₊ + $\frac{1}{2}$ H₂ \uparrow

$$R-SH \xrightarrow{Na} RSNa + \frac{1}{2}H_2 \uparrow$$

PhOH
$$\xrightarrow{\text{Na}}$$
PhONa + $\frac{1}{2}$ H₂ \uparrow

(f) R—SO₃H + Na
$$\rightarrow$$
 R—SO₃-Na⁺ + $\frac{1}{2}$ H₂ ↑

(h) R—CH=CH₂ + Na
$$\rightarrow$$
 No reaction.

(i)
$$HCI \xrightarrow{Na} NaCI + \frac{1}{2}H_2 \uparrow$$

(2) Test for unsaturation:

(i) Bromine water test (Br₂ + H₂O, Red-brown solution):

This is used to distinguish between saturated (alkane) and unsaturated (alkene/alkyne) hydrocabon.

$$\begin{array}{c} R-CH_2-CH_3 \xrightarrow{Br_2,H_2O} & \text{no reaction} \\ R-CH-CH_2 \\ R-CH = CH_2 \xrightarrow{Br_2,H_2O} & Br & Br \\ & & & \\ Br & Br \\ & & & \\ R-C-C-R \\ & & \\ R-C = CR \xrightarrow{Br_2,H_2O} & Br & Red-brown colour disappears \\ \end{array}$$

Note: Phenol and aniline reacts with bromine water but benzene does not react.

(ii) Baeyer reagent (Cold dil. alkaline KMnO₄ Pink/purple solution):

This is also used to distinguish between saturated (alkane) and unsaturated (alkene/alkyne) compounds.

$$\begin{array}{c} \text{R-CH}_2\text{-CH}_3 & \xrightarrow{\text{Cold, dil.KMnO}_4} & \text{no reaction} \\ \\ \text{R-CH} = \text{CH}_2 & \xrightarrow{\text{Cold, dil.KMnO}_4} & \text{OH OH Purple colour disappears} \\ \\ \text{R-C-C-R} & & \parallel \parallel \\ \\ \text{R-C} = \text{CR} & \xrightarrow{\text{Cold, dil.KMnO}_4} & \text{O O} & \text{Purple colour disappears} \\ \\ \hline \text{2KMnO}_4 & \xrightarrow{\Rightarrow} \text{K}_2\text{O} + 2\text{MnO}_2 + 3 \text{ [O]} \\ & \text{Brown solution} \\ \end{array}$$

(3) Test for terminal Alkyne

(i) Tollen's reagent [AgNO₃ + NH₄OH or {Ag(NH₃)₂}₊OH₀]:

Tollen's Reagent gives white precipitate (Silver alkynide) with terminal alkyne.

$$R-C \equiv CH \xrightarrow{AgNO_3+NH_4OH} R-C \equiv CAg + NH_4NO_3$$
White precipitate

(ii) Ammonical cuprous chloride (Cu₂Cl₂ + NH₄OH):

It gives red precipitate with terminal alkyne.

2 R-C
$$\equiv$$
 CH $\xrightarrow{\text{Cu}_2\text{Cl}_2+\text{NH}_4\text{OH}}$ 2 R-C \equiv CCu \downarrow + 2NH₄Cl + 2H₂O Red precipitate

Section (D): Test for Functional groups

(4) Test for alcohols:

- (i) Lucas reagent test (Conc. HCl + anhydrous ZnCl₂)
- * It gives white turbidity or cloudiness with alcohols (OH groups attached with sp³ hybridised carbon).
- * Lucas Reagent is used to distinguish between 1°, 2°, 3° alcohol because 1°, 2°, 3° alcohols react with different rates.

(a) 1° alcohol R-CH₂-OH
$$\xrightarrow{\text{conc. HCl+anhydrous } ZnCl_2}$$
 R-CH₂-CI (does not give appreciable reaction or gives white turbidity in 30 min.)

(b) 2° alcohol R₂CH-OH
$$\xrightarrow{\text{conc. HCl+anhydrous } ZnCl_2}$$
 R₂CH-Cl (gives white turbidity in 5 min. $\frac{1}{2}$

(c) 3° alcohol R₃C-OH
$$\xrightarrow{\text{conc. HCl+anhydrous ZnCl}_2}$$
 R₃C-CI (gives white turbidity immediately)

(ii) Victor Mayer test:

1° Alcohol%

$$RCH_{2}-OH \xrightarrow{P+I_{2}} RCH_{2}-I \xrightarrow{AgNO_{2}} RCH_{2}-NO_{2} \xrightarrow{HNO_{2}} R-C=N-OH \xrightarrow{base} Blood Red colour$$

$$2^{\circ} Alcohol\% \qquad R_{2}CH-OH \xrightarrow{P+I_{2}} R_{2}CH-I \xrightarrow{AgNO_{2}} R_{2}CH-NO_{2} \xrightarrow{HNO_{2}} R_{2}C-NO_{2} \xrightarrow{base} Blue colour$$

$$3^{\circ} Alcohol\% \qquad R_{3}C-OH \xrightarrow{P+I_{2}} R_{3}C-I \xrightarrow{AgNO_{2}} R_{3}C-NO_{2} \xrightarrow{HNO_{2}} no reaction \xrightarrow{base} no colour$$

(iii) Cerric Ammonium Nitrate test : (Group reagent for alcohols)

Alcohols(1°,2°,3°) also give characteristic red colour with cerric ammonium nitrate $(NH_4)_2[Ce(NO_3)_6]$ solution.

(5) Test for phenol or enol:

Neutral FeCl₃ test:

It forms coloured complex with phenol or enol (OH groups attached with sp² carbon).

6 PhOH + FeCl₃
$$\longrightarrow$$
 $[(PhO)_6 Fe]^{3-} + 3HCl + 3H^+$
(Coloured complex)

(6) Test for carbonyl compounds:

^{*} Phenols and enols do not give Lucas test.

^{*} It does not give positive test with alcohol.

2, 4-DNP 1/42, 4-Dinitrophenyl hydrazine-1/2 Test:

Carbonyl compouds (all aldehydes and ketones) give yellow–orange precipitate with 2,4–DNP. It is also knwon as **Brady's reagent**.

$$C = O + H_2N - NH \longrightarrow NO_2 \longrightarrow C = N - NH \longrightarrow NO_2$$

$$0 \times NO_2 \longrightarrow NO_2$$

(7) Test for aldehydes:

(a) Tollen's reagent [AgNO₃ + NH₄OH or {Ag(NH₃)₂}₊OH₀]:

Tollen's Reagent gives silver mirror or Black precipitate with aldehydes.

$$R-CH = O \xrightarrow{AgNO_3+NH_4OH} R-C-O^{\Theta} + Ag \downarrow$$
silver mirro

Note: HCOOH also gives this test.

(b) Fehling's solution:

It is an alkaline solution of cupric ion complexed with sodium potassium tartarate.

There are two solutions in Fehling solution,

Solution (A): CuSO₄ solution and

Solution (B): Alkaline solution of sodium potassium tartarate.

When these two solutions are mixed we get deep blue coloured solution.

CuSO₄ + 2NaOH
$$\rightarrow$$
 Cu(OH)₂ + Na₂SO₄
HO - CH - COONa
HO - CH - COOK
Cu(OH)₂ + रॉशेल लवण \rightarrow (मीले रंग का यौगिक)
Roschelle salt (Blue coloured compound)

Equal volume of both the solutions are heated with aldehyde to give red brown precipitate of cuprous oxide (Cu₂O) which confirms the presence of aldehyde.

R-CHO + Blue
$$\rightarrow$$
 RCOOH + Cu₂O (Red ppt)
RCHO + 2Cu²⁺ + 3OH \rightarrow RCOO + (Red ppt) + 2H₂O

(c) Benedict solution:

It also consists of two solutions.

Solution (A): CuSO₄ -→ solution and

Solution (B): Alkaline solution of sodium Citrate.

$$\begin{array}{c|c} & CH_2COONa \\ & CH_2COONa \\ & | \\ & | \\ HO-C-COONa \\ & | \\ CU(OH)_2 + & CH_2-COONa_{-\rightarrow} \end{array} \\ \begin{array}{c|c} & CH_2COONa \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & |$$

Aldehyde gives positive test with Benedict solution.

$$2Cu^{2+}$$
 $2Cu^{\oplus} + 2H_2O$
RCH = O + (blue) + $3OH^{\ominus}$ - \rightarrow RCOO + (Red ppt.)

(d) Schiff's reagent :

It is dilute solution of rosaniline hydrochloride whose pink colour has been discharged by passing SO_2 . Aldehyde restores pink colour when treated with schiff's reagent (Magenta solution in H_2SO_3).

Benzaldehyde does not gives Fehling, Bendict & Schiff's test

* Aromatic aldehydes (Benzaldehyde) do not gives Fehling and Bendict test.

(8) lodoform test:

Reagents : I_2 + NaOH or NaOI $\frac{1}{4}$ Where R = H, alkyl, aryl group $\frac{1}{2}$

Acetaldehyde, all methyl ketones & ethyl alcohol give lodoform test.

$$R-C-CH_{3} \xrightarrow{I_{2}+NaOH} R-C-ONa + CHI_{3} \downarrow$$

$$R-COOH$$

$$(Acid of 1 carbon less)$$

$$OH$$

$$R-CH-CH_{3} \xrightarrow{I_{2}+NaOH} R-C-ONa + CHI_{3} \downarrow$$

$$H$$

$$Y=0$$

(9) Test for acids/esters/amides:

(i) Sodium bicarbonate test (NaHCO₃) %

All the acids which are stronger than H₂CO₃ give CO₂ gas with NaHCO₃.

Note : (i) If electron withdrawing group (NO₂) is present at ortho or para position of phenol then it gives positive test with sodium bicarbonate.

(ii) Litmus test % Acid converts blue litmus into red litmus while base converts red litmus into blue.

Test for Acid amide: Gives smell of ammonia when heated with alkali.

$$\begin{array}{c}
O \\
| | \\
R-C-NH_2 \xrightarrow{NaOH} R-C-ONa + NH_3
\end{array}$$

Test for Esters : Esters are sweet (fruity) smelling liquids.

When react with NaOH & Phenophthalein then pink colour will disappear on heating.

RCOOR' + NaOH + Phenophthalein (Pink) $\stackrel{\Delta}{\longrightarrow}$ R COOH + R' OH (Colourless solution)

(10) Test for amines:

(i) NaNO₂ + aqueous HCl test % it is used to distinguish between 1°, 2° and 3° amines and also distinguish between aliphatic and aromatic primary amines.

1° Aromatic Amine :
$$Ph-NH_2 \xrightarrow{NaNO_2 + aq. \ HCl} Ph-N_2^+Cl$$
 1/4 diazonium salt/

(ii) Carbyl amine test (CHCl₃ + KOH)

1° Amine (Aliphatic or Aromatic) %

(iii) Hofmann mustard oil test:

It is a test for 1° amine and aniline. Primary amine reacts with carbon disulphide to form dithioalkyl carbamic acids which decompose on heating with mercuric chloride (HgCl₂) to give alkyl isothiocyanates having smell like mustard oil.

(a)
$$R-NH_2+S=C=S \longrightarrow R-NH-S \xrightarrow{\Delta} R-N=C=S+HgS+2HCI$$
Dithioethylcarbamic acid Alkylisothiocyanate

(b) $CH_3CH_2NH_2+S=C=S \xrightarrow{\Delta} CH_3CH_2NH-C-SH \xrightarrow{\Delta} CH_3CH_2-N=C=S+HgS+2HCI$
(1° amine)

Ethyl isothiocyanate

Similarly aniline gives phenlyisothiocyanate
(i) S=C=S

CHN=C=S

(c)
$$C_6H_5NH_2$$
 (ii) $HgCl_2/\Delta$ Phenylisothiocyanate

* 2° Amine and 3° Amine do not give this test.

(iv) Hinsberg reagent (C₆H₅SO₂CI):

This is used to distinguish between 1°,2° & 3° amine.

2° Amine:
$$R_2NH + PhSO_2CI \xrightarrow{Pyridine} R_2N-SO_2-Ph \xrightarrow{Base}$$
 Compund is **insoluble** in base.

3° Amine: R₃N PhSO₂Cl — Pyridine → No reaction.

(11) Test of nitro group : (Mulliken-Barker's test)

Nitroalkane & nitrobenzene give black ppt on reduction with Zn and ammonium chloride followed by treating with Tollen's reagent. **This is also said to be Mulliken's test.**

(a)
$$R-NO_2$$
 $\xrightarrow{\Delta}$ $Ag \downarrow$ A

(12) Test for carbohydrates & sugars

^{* 2°} Amine and 3° Amine do not give this test.

Molisch test:

This is a general test for carbohydrates. One or two drops of alcoholic solution of α -naphthol is added to 2 ml glucose solution. 1 ml of conc. H_2SO_4 solution is added carefully along the sides of the test tube. The formation of a violet ring at the junction of two liquids confirms the presence of a carbohydrate or sugar.

(13) Test for amino acids and proteins:

Ninhydrin Test: This is used to detect the presence of amino acids & proteins.

Section (E): Elements detection

(1) Detection of carbon and hydrogen:

Carbon and hydrogen are detected by heating the compound with copper(II) oxide. Carbon present in the compound is oxidised to carbon dioxide (tested with lime-water, which develops turbidity) and hydrogen to water (tested with anhydrous copper sulphate, which turns blue).

$$C + 2CuO \xrightarrow{\Delta} 2Cu + CO_2 \qquad ; \qquad 2H + CuO \xrightarrow{\Delta} Cu + H_2O$$

$$CO_2 + Ca(OH)_2 \xrightarrow{\Delta} CaCO_3 \downarrow + H_2O \qquad ; \qquad 5H_2O + CuSO_4 \xrightarrow{\Delta} CuSO_4.5H_2O$$

$$White \qquad Blue$$

(2) Detection of other elements:

Nitrogen, sulphur, halogens and phosphorus present in an organic compound are detected by "Lassaigne's test". The elements present in the compound are converted from their covalent form to their ionic form by fusing the organic compound with sodium metal.

Following reactions take place: C, N, S and X come from organic compound.

Cyanide, sulphide and halide of sodium so formed on sodium fusion are extracted from the fused mass by boiling it with distilled water. This extract is known as sodium fusion extract or Lassaigne solution.

$$Na + C + N \xrightarrow{\Delta} NaCN$$

$$2Na + S \xrightarrow{\Delta} Na_2S$$

$$Na + X \xrightarrow{\Delta} NaX$$

$$Na + C + N + S \xrightarrow{\Delta} NaSCN$$

(i) Test for nitrogen:

The sodium fusion extract is boiled with iron(II) sulphate and then acidified with dilute sulphuric acid. The formation of Prussian blue or green colour confirms the presence of nitrogen. Alternatively FeCl₃ and dil. HCl may be added.

6NaCN + FeSO₄
$$\rightarrow$$
 Na₄[Fe(CN)₆]
Na₄[Fe(CN)₆] + 4Fe³⁺ $\xrightarrow{xH_2O}$ Fe₄[Fe(CN)₆]₃. xH₂O
Ferric ferrocyanide (Prussian blue)

(ii) Test for sulphur

(a) The sodium fusion extract is acidified with acetic acid and lead acetate is added to it. A black precipitate of lead sulphide indicates the presence of sulphur.

$$Na_2S + (CH_3COO)_2Pb - \rightarrow PbS$$

Black

(b) On treating sodium fusion extract with sodium nitroprusside, appearance of a violet colour indicates the presence of sulphur.

$$Na_2S + Na_2[Fe(CN)_5NO] - \rightarrow Na_4[Fe(CN)_5NOS]$$

Sodium nitroprusside

Sodium thionitroprusside (Violet/Purple)

(c) In case, nitrogen and sulphur both are present in an organic compound, then sodium thiocyanate is formed. It gives blood red colour with neutral FeCl₃.

Na + C + N + S
$$\rightarrow$$
 NaSCN
Neutral FeCl₃ + NaSCN \rightarrow Fe(SCN)₃
Blood red

(iii) Test for halogens:

The sodium fusion extract is acidified with nitric acid and then treated with silver nitrate. A white precipitate, soluble in ammonium hydroxide shows the presence of chlorine, a yellowish precipitate, sparingly soluble in ammonium hydroxide shows the presence of bromine and a yellow precipitate, insoluble in ammonium hydroxide shows the presence of iodine.

Note: The sodium fusion extract is first boiled with concentrated nitric acid to decompose cyanide or sulphide of sodium formed during Lassaigne's test. These ions would otherwise interfere with silver nitrate test for halogens.

(iv) Test for phosphorus:

The compound is heated with an oxidising agent (sodium peroxide). The phosphorus present in the compound is oxidised to phosphate. The solution is boiled with nitric acid and then treated with ammonium molybdate. A yellow-white colouration or precipitate indicates the presence of phosphorus.