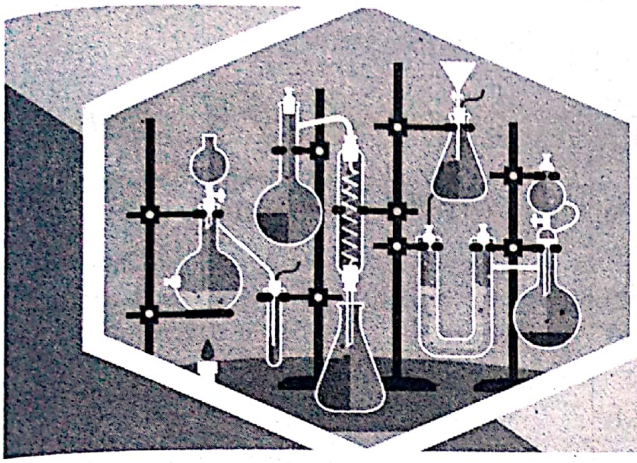


Qualitative Analysis of Single Solid Organic Compounds

Chapter 5

5.1 Basic Concepts

Organic compounds are composed of carbon. Apart from carbon hydrogen, oxygen, nitrogen, sulphur and halogens are commonly occurring elements in organic compounds. A number of functional groups are also usually present in organic compounds. Finding out the identity of the special elements and the functional groups leading to the identification of the compound is the goal of qualitative organic analysis. A compound is characterised by determination of its melting point, identification of the special elements and functional groups present in it, checking of solubility and preparation of suitable derivatives.

5.1.1 Detection of Special Elements (N, S, Cl, Br, I) [Lassaigene's test]

A small amount of the sample is strongly fused with a pea sized sodium in a fusion tube until the bottom of the tube becomes red hot. The tube is then broken with a pestle into ~ 10 ml of distilled water contained in a mortar. The mixture is ground thoroughly with the pestle. The mixture is then filtered. The filtrate, known as sodium extract, is used for the following tests.

Experiment	Observation	Inference
1. *Test for Nitrogen* A little of the filtrate is boiled with a pinch* of solid ferrous sulphate or Mohr's salt, cooled and acidified with 6(N) sulphuric acid.	Blue or green colouration or precipitate.	N present
2. *Test for Halogen* A little of the filtrate is boiled with conc. Nitric acid. The solution is cooled and treated with a few drops of silver nitrate solution.	i. Curdy white precipitate soluble in excess ammonium hydroxide. ii. Pale yellow precipitate iii. yellow precipitate	i. Cl present ii. Br present iii. I present
3. *Test for Iodine* A little of the filtrate is boiled with conc. Nitric acid. Carbon tetrachloride is added to it. Then the mixture is shaken vigorously with chlorine water.	Carbon tetrachloride layer turns violet	I present

Experiment	Observation	Inference
4. *Test for Bromine* The mixture is test no. 3 is continued to be shaken with chlorine water until the violet colour of the carbon tetrachloride layer disappears. Addition of chlorine water and shaking are continued.	Carbon tetrachloride layer turns reddish brown	Br present
5. *Test for Sulphur* A few drops of sodium nitroprusside solution is added to a small portion of the filtrate.	Violet or purple colouration	S present

* ***Blackening of the filtrate on addition of ferrous sulphate indicates the presence of sulphur. In such cases excess ferrous sulphate needs to be added for successful detection of Nitrogen.***

■ **Reactions :**

① ***Detection of Nitrogen*** **:**

$Na + C + N \rightarrow NaCN$,

$NaCN + FeSO_4 \rightarrow Na_4[Fe(CN)_6]$,

$Na_4[Fe(CN)_6] + Fe^{3+} \rightarrow Fe_4[Fe(CN)_6]_3$ (Prussian blue) [*Ferric salt is produced by aerial oxidation of ferrous sulphate*]

② ***Detection of Halogens*** **:**

$Na + X \rightarrow NaX$ (X = Cl, Br, I), $NaX + AgNO_3 \rightarrow NaNO_3 + AgX$ (Curdy white for X = Cl, Pale yellow for X = Br, Yellow for X= I)

$AgCl + NH_4OH \rightarrow Ag(NH_3)_2Cl$ (soluble)

$NaI + Cl_2 \rightarrow I_2$(Violet organic layer) $+NaCl$

$NaBr + Cl_2 \rightarrow Br_2$(Reddish brown organic layer) $+ NaCl$

③ ***Detection of Sulfur*** **:**

$Na + S \rightarrow Na_2S$ $\quad\quad$ $Na_2S + Na_2[Fe(CN)_5(NO)] \rightarrow Na_4[Fe(CN)_5(NO)S]$ (Purple colour)

5.1.2 Detection of Functional Groups

Experiment	Observation	Inference
1. *Test for* $-COOH$ *group*[#] *:* A pinch of the given sample is added to a saturated solution of $NaHCO_3$.	Effervescence observed	$-COOH$ present
2. *Test for* $-COOH$ *group:* The given sample is heated with ethanol and 2-3 drops concentrated sulphuric acid and the solution is poured in large excess of water.	Sweet smell is perceived	$-COOH$ present
3. *Test for phenolic* $-OH$ *group*[##]*:* A few drops of freshly prepared solution of ferric chloride is added to an aqueous or ethanolic solution of the sample.	Violet or green or blue or red colouration	Phenolic $-OH$ present

Experiment	Observation	Inference
4. *Test for phenolic —OH group: Back-dye test*:* The given sample is dissolved in dilute sodium hydroxide solution. An HCl solution of aniline is prepared and cooled in ice. A cold, saturated solution of sodium nitrite is added to the ice-cold HCl solution of aniline. The resulting solution is then added to the ice-cold, alkaline solution of the sample.	Brilliant orange or red dye	Phenolic —OH present
5. *Test for carbonyl group:* 2,4-D.N.P. solution is added to an ethanolic solution of the sample.	Yellow or orange precipitate [If no precipitate is formed simply on mixing the two solutions the mixture has to be heated on a water bath for ~5 minutes. Then water has to be added drop wise to it followed by scratching of the inner wall of the test tube with a glass rod]	Carbonyl group present
6. *Test for —CHO group (to be performed only if the carbonyl group is present) :* An ethanolic solution of the sample is added to Tollen's reagent and the test tube is heated on a water bath for ~5 minutes.	Black or grey precipitate or shining silver mirror.	—CHO or α-hydroxy keto group present
7. *Test for olefinic unsaturation:* A few drops of very dilute potassium permanganate solution is added to an ethanolic solution of the sample.	Pink colour of permanganate disappears	Olefinic unsaturation or easily oxidisable group present
8. *Test for aromatic $-NH_2$ group :* The given sample is dissolved in excess of dilute hydrochloric acid. The solution is cooled in ice and a cold, saturated solution of sodium nitrite is added to it. The resulting solution is then added to an ice-cold, alkaline solution of β-naphthol.	Brilliant orange or red dye	Aromatic $-NH_2$ group present
9. *Test for $-NO_2$ group (Mulliken Barker Test):* An aqueous ethanolic solution of the given sample is boiled with zinc dust and solid ammonium chloride. The mixture is cooled and filtered into Tollen's reagent.	Black or grey precipitate or shining silver mirror	$-NO_2$ group present

Experiment	Observation	Inference
10. *Test for* $-NO_2$ *group (in absence of aromatic* $-NH_2$*) :* The given sample is boiled with a granule of tin and concentrated hydrochloric acid. The mixture is diluted with water and ice-cooled. A cold, saturated solution of sodium nitrite is added to this solution. The resulting solution is added to an ice-cold, alkaline solution of β-naphthol.**	Brilliant orange or red dye	$-NO_2$ group present
11. *Test for* $-CONH_2$ *or imide group :* The given sample is heated with 2-3 beads of solid sodium hydroxide.	Smell of ammonia perceived	Amide $-CONH_2$ or imide ($-CONHCO-$) group present
12. *Test for* $-CONHAr$ *(anilido) group :* The given sample is heated with Concentrated hydrochloric acid. The solution is diluted with water and ice-cooled. A cold, saturated solution of sodium nitrite is added to this solution. The resulting solution is added to an ice-cold, alkaline solution of β-naphthol.***	Brilliant orange or red dye	$-CONHAr$ group present

Some acidic compounds such as nitrophenols, amine hydrochlorides, sulfonic acids etc. also respond to this test.

##

- β-naphthol gives green colouration
- Hydroquinone gives transient green colouration
- Catechol gives blue colouration
- *p*-Nitro phenol gives red colouration (*this test is best accomplished in aqueous solution of p-nitro phenol*)
- Not all phenols respond to $FeCl_3$ test, *e.g, o*-nitro phenol, *o*- and *m*-aminophenol, 2,4 -diaminophenol, *m*- and *p*-hydroxybenzoic acids do not give any colour when treated with $FeCl_3$ solution.
- In contrast, some aromatic primary amines *e.g. p*-anisidine, *o*-, *m*- and *p*-aminobenzoic acid, sulphanilic acid etc. give characteristic reddish-violet/violet colouration on treatment with $FeCl_3$.

* *Not all phenols respond to back dye test. Specially phenols whose ortho and para positions are blocked do not undergo this reaction. So ferric chloride test may be used as the more reliable test for phenolic* $-OH$.

** *In the presence of* $-NH_2$ *group, the* $-NO_2$ *group has to be identified only by Mulliken Barker test.*

*** *In presence of aromatic amines the test for anilido group need not be performed. The conclusion will be written as follows: "As aromatic amino group is present test for anilido group is not performed".*

■ Reactions :

◗ *Test for* $-COOH$ *group :*

① $RCOOH + NaHCO_3 \rightarrow RCOONa + CO_2$(responsible for effervescence) $+ H_2O$

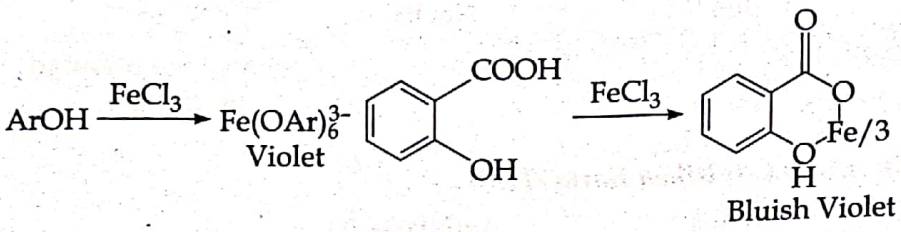
Other acidic compounds such as nitrophenols, amine hydrochlorides, sulfonic acids etc also respond to this test.

② $RCOOH + EtOH + H_2SO_4 \rightarrow RCOOEt$ (responsible for sweet smell)

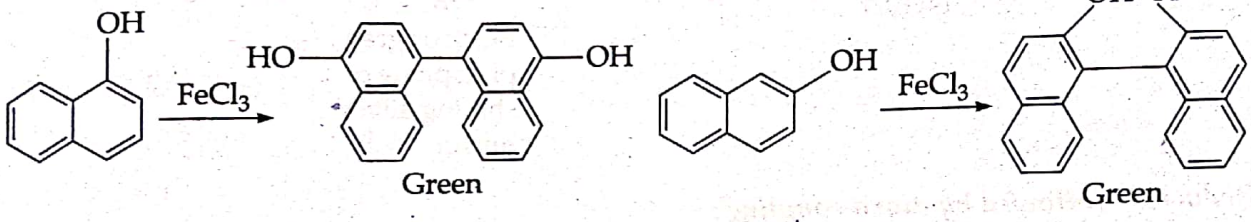
◗ *Test for phenolic —OH group :*

① *Ferric chloride test :*

Different phenols react differently with ferric chloride. Some representative examples are given below.

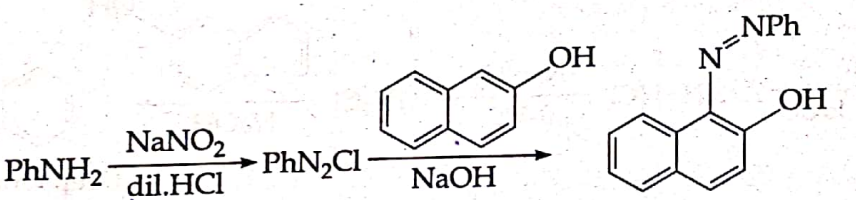


Bluish Violet



Green

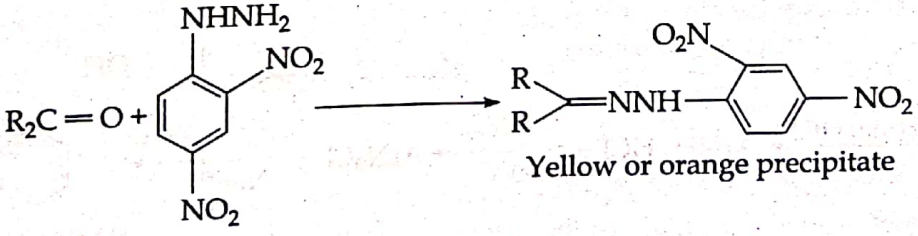
② *Back dye test :*



Deep Orange coloured precipitate

◗ *Test for carbonyl group:*

① 2,4-D.N.P. test



Yellow or orange precipitate

② *Test for —CHO group (Tollen's test)*

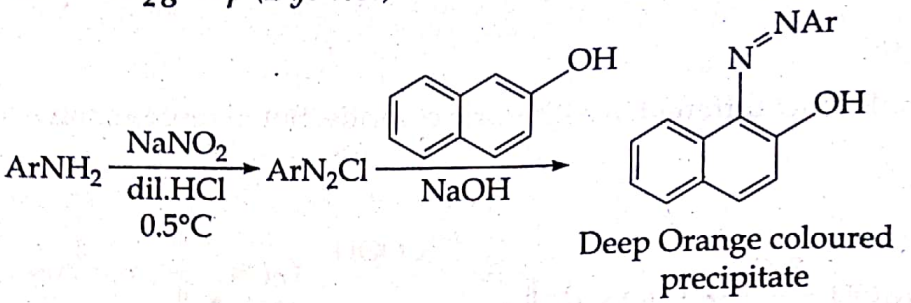
$RCHO + Ag(NH_3)_2OH \rightarrow RCOONH_4 + Ag$ (responsible for grey or black precipitation or silver mirror) $+ H_2O + NH_3$

◗ *Test for Olefinic unsaturation:*

$$R_2C{=}CR_2 + KMnO_4 \rightarrow R_2C(OH)-C(OH)R_2$$

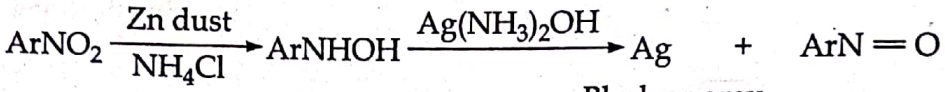
Compounds containing easily oxidisable group such as phenolic —OH, amines or certain dicarboxylic acids like oxalic acid also respond to this test.

- *Test for aromatic* $-NH_2$ *group (Dye test) :*



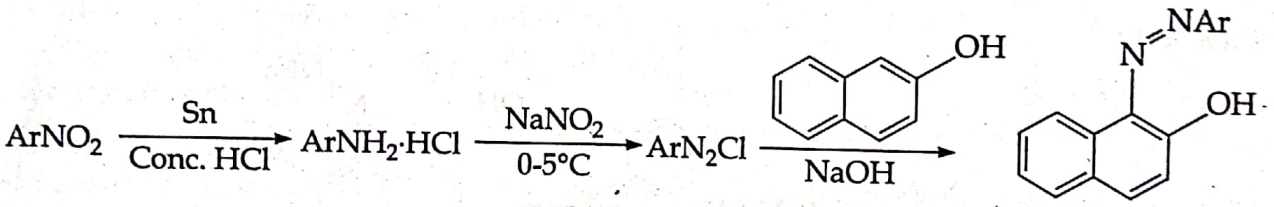
Deep Orange coloured precipitate

- *Test for* $-NO_2$ *group (Mulliken BarkerTest) :*



Black or grey precipitate or shining silver mirror

- *Reduction followed by diazo coupling :*

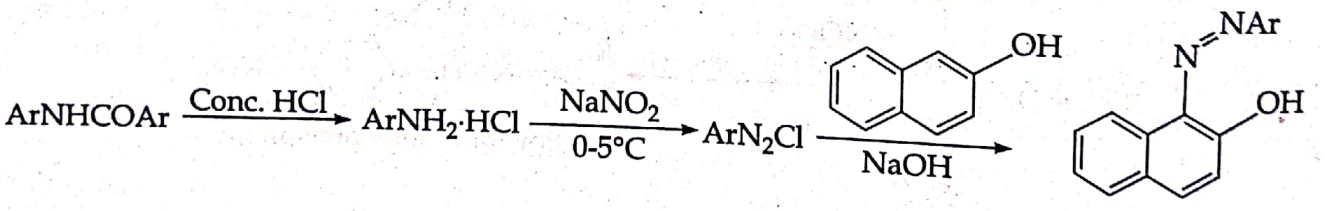


Deep Orange coloured precipitate

- *Test for* $-CONH_2$ *group :*

$$RCONH_2 + NaOH \rightarrow RCOONa + NH_3$$

- *Test for* $-CONHAr$ *(anilido)group :*



Deep Orange coloured precipitate

5.1.3 Solubility Test and Classification Based on Solubility

Solubility of the given sample needs to be examined in water, dilute HCl, dilute NaOH and saturated $NaHCO_3$ solution.

~ 0.25 mg of the sample (preferably in powdered form, if crystalline sample is given,it should be ground thoroughly with the pestle to convert into the powdered form) is vigorously shaken with 2 ml of each of the following solvent at room temperature. The result should be reported in the following tabular form.

Water	Dilute HCl	Dilute NaOH	Saturated $NaHCO_3$ solution
'✓'or '×'	'NP' or '✓' or '×'	'NP' or '✓' or '×'	'NP' or '✓' or '×'

NP = not performed, × = insoluble, ✓ = soluble

Following combinations are possible

Water	Dilute HCl	Dilute NaOH	Saturated $NaHCO_3$ solution	Remarks / Conclusion
✓	NP	NP	NP	Inconclusive with respect to the nature of the functional groups. [*If the sample is soluble in water its solubility in the other solvents need not be checked*]
×	✓	×	NP	Basic functional group e.g. Aromatic amine may be present
×	×	✓	✓	Strongly acidic group e.g. -COOH, $-SO_3H$ may be present. [*If the sample is insoluble in dil. NaOH solution, solubility in saturated $NaHCO_3$ solution need not be checked*]
×	×	✓	×	Weekly acidic group e.g.phenolic -OH, imide may be present.
×	✓	✓	✓	Basic and strongly acidic functional groups are present *e.g.* amino acids, sulphanilic acid etc.
×	✓	✓	×	Basic and weakly acidic functional groups are present e.g.amino phenols etc.
×	×	×	NP	The nature of the functional group is neither acidic nor basic. If N is present as special element, the sample may contain aromatic NO_2/amide/anilido group If N is absent as special elements, it may contain carbonyl group

5.1.4 Literature Survey

Identification of special elements and functional groups followed by accurate determination of melting point of the given solid organic sample gives a clue to the identity of the unknown compound. However, a number of functionally identical compounds may have close melting points. Therefore, the unknown sample needs to be suitably derivatised and melting points of the prepared derivatives have to be compared with the melting points of the same derivatives of the suspected compound. Compatibility of the melting points of the compounds and their suitable derivatives may safely lead to the identification of the unknown compound.

From .....(Title of the book) by.....(author name)

Special Element present	Functional group present	Observed Melting Point	Compound(s) in the literature melting point within ± 10 °C	Possible derivative(s) with melting point

5.1.5 Preparation of Derivatives

After identification of the special element and the functional group the compound under investigation needs to be suitably derivatised for its identification.

Functional group	Derivative
Phenolic –OH	Benzoyl
Aromatic $-NH_2$	Acetyl, Benzoyl
Carbonyl	2,4-DNP, Semicarbazone, Oxime
Carboxylic acid	SBT, Amide, Anilide
Aromatic NO_2	Poly Nitro
Amido	Hydrolysis
Anilido	Bromo, Nitro

- **Benzoyl Derivative (Suitable for Phenolic –OH and Aromatic amines) :** About 1g of the amine is dissolved in minimum volume of acetone in a 100 ml dry conical flask. 10 ml of 10% sodium hydroxide solution is added to it. (In case of phenolic –OH the sample may be directly dissolved in 10% sodium hydroxide solution and use of acetone should be omitted). About 1-1.5 ml of benzoyl chloride is added slowly with constant stirring to the alkaline solution of the sample. The flask is corked tightly and shaken vigorously with occasional cooling in an ice-cold water bath. Shaking is continued till the disappearance of the odour of benzoyl chloride. If needed more NaOH solution needs to be added. The precipitated product is filtered off, washed thoroughly with water and recrystallised from aqueous ethanol. (If the sample contains an acidic functionality acidification of the reaction mixture is required finally to obtain the benzoylated derivative)

$$Ar\text{-}OH + PhCOCl + NaOH \rightarrow ArOCOPh + NaCl + H_2O$$

$$Ar\text{-}NH_2 + PhCOCl + NaOH \rightarrow ArNHCOPh + NaCl + H_2O$$

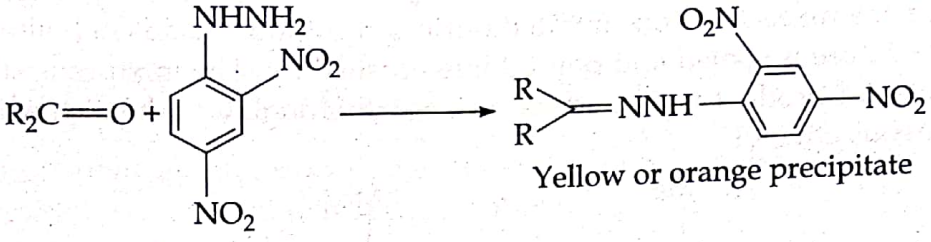
- **Acetyl Derivative (Suitable for Aromatic amines) :** About 1 g of the amine is dissolved in minimum volume of acetone in a dry test tube, cooled in an ice bath and to it 1 ml of pyridine is added. ~ 1ml of acetyl chloride is added slowly to the amine solution with stirring. The reaction mixture is heated on a water bath for 10 minutes. The whole content of the test tube is then poured into crushed ice and stirred well with a glass rod. The precipitated product is filtered off, washed thoroughly with cold water and recrystallised from aqueous ethanol.

$$Ar\text{-}NH_2 + CH_3COCl \rightarrow ArNHCOCH_3 + HCl$$

- *Alternative Green Method*

~ 0.5 g of hydrated sodium acetate is dissolved in 5 ml of brine solution (saturated aqueous solution of sodium chloride). ~ 0.5 g of amine is dissolved in minimum volume of acetone and poured into the above solution.1 ml of acetyl chloride is added to the mixture drop-wise with stirring. The reaction mixture is stirred for further 25-30 minutes. Then saturated solution of $NaHCO_3$ is added to the reaction mixture till the effervescence ceased followed by acidification with conc. HCl. The precipitated product is filtered off, washed thoroughly with water and recrystallised from aqueous ethanol. (If the sample contains an acidic functionality neutralisation is required prior to acetylation. This is done by adding solid Na_2CO_3 portion-wise in a warm aqueous suspension of the substrate amine. After complete addition of Na_2CO_3, a clear solution result, into which the above method is applied).

■ **2,4-DNP derivative (Suitable for Carbonyl group) :** 0.25 g of 2,4-dinitro phenyl hydrazine hydrochloride is added to 5 ml of methanol and stirred well with a glass rod. 0.5 -1 ml of conc. sulphuric acid is added to it. If the solution is still not clear it is filtered and the filtrate is added to a solution of 0.5 g of the sample dissolved in minimum volume of ethanol. The mixture is shaken thoroughly and if the product does not separate within 5 minutes water is added dropwise to the reaction mixture and warmed on a water bath. The precipitated product is filtered off, washed thoroughly with ethanol and recrystallised from absolute alcohol.



Yellow or orange precipitate

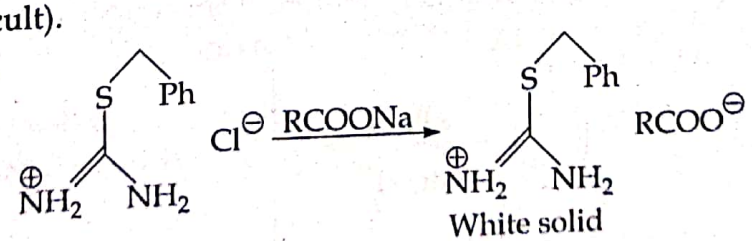
■ **Semicarbazone derivative (Suitable for Carbonyl group) :** About 0.8 g of hydrated sodium acetate and 0.5 g of semicarbazide hydrochloride are dissolved in 5 ml of water.0.5g of the sample is dissolved in minimum volume of ethanol and the ethanolic solution is added to the aqueous solution of semicarbazide hydrochloride and sodium acetate. The mixture is shaken vigorously and allowed to stand until the product separates. (In some cases several hours may be needed). Sometimes the reaction may be hastened by gentle heating on a water bath for up to 20 minutes followed by cooling in ice water. The precipitated product is filtered off, washed thoroughly with cold water and recrystallised from aqueous ethanol.

$$R_2C{=}O + H_2NNHCONH_2 \rightarrow R_2C{=}NNHCONH_2$$

■ **Oxime derivative (Suitable for Carbonyl group) :** The same method may be applied as described under semicarbazone derivative. Instead of semicarbazide hydrochloride 1 g of hydroxylamine hydrochloride has to be used. Weight of sodium acetate may be increased up to 2 g.

$$R_2C{=}O + H_2NOH \rightarrow R_2C{=}NOH$$

■ **S-Benylthiouronium (SBT) derivative (suitable for Carboxylic acid) :** About 0.5 g of the sample is dissolved in 6-8 ml of a saturated aqueous solution of sodium bicarbonate. The solution is added to a solution of 1.5 g of S-benzylthiouronium chloride in 5 ml water contained in a 50 ml beaker. If the product does not separate immediately the reaction mixture is cooled in ice and scratched thoroughly with a glass rod. The precipitated product is filtered off, washed thoroughly with cold water and recrystallised from aqueous ethanol. (Recrystallisation may sometimes be difficult).



White solid

■ **Amide derivative (suitable for Carboxylic acid) :** 1 g of the sample is refluxed with 3 ml of thionyl chloride for 30 minutes in a fume chamber or until no further reaction takes place. Excess of thionyl chloride is removed by distillation. The cold acid chloride is added dropwise to cold liquor ammonia and warmed for a few minutes. The precipitated product is filtered off, washed thoroughly with cold water and recrystallised from aqueous ethanol.

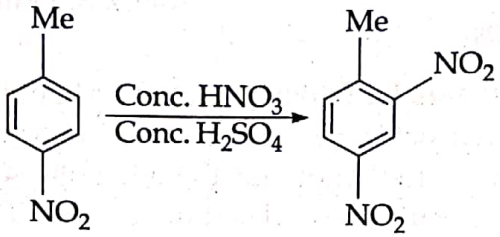
$$RCOOH + SOCl_2 \rightarrow RCOCl$$

$$RCOCl + NH_3 \rightarrow RCONH_2$$

■ **Anilide derivative (suitable for Carboxylic acid) :** Same method as described under the preparation of amide derivative may be adopted replacing ammonia by 1 ml of aniline. In this case washing of the product with dilute hydrochloric acid is needed to remove the unreacted aniline.

$$RCOOH + SOCl_2 \rightarrow RCOCl$$
$$RCOCl + PhNH_2 \rightarrow RCONHPh$$

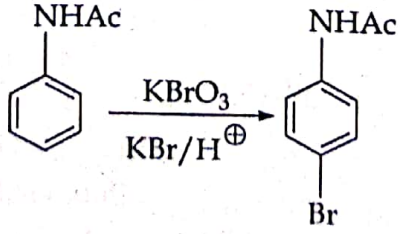
■ **Nitro derivative (Suitable for compounds containing only $-NO_2$ group) :** 1 g of the sample is heated with a mixture of 4 ml each of concentrated nitric and sulphuric acids in boiling water for 30-50 minutes. The mixture is cooled and poured into crushed ice. The mixture is stirred well till the ice melts. The solid product is filtered off, washed thoroughly with cold water and recrystallised from aqueous ethanol.



■ **Derivative by hydrolysis (suitable for Amides) :** 1 g of the sample is heated with 25 ml of 20% sodium hydroxide solution in a 100 ml conical flask for 30 minutes or until the disappearance of the smell of ammonia. During the heating an inverted funnel is placed on the conical flask and water is added from time to time if the solution evaporates too quickly. The reaction mixture is cooled and acidified with concentrated hydrochloric acid. The solid product is filtered off, washed thoroughly with cold water and recrystallised from aqueous ethanol or water.

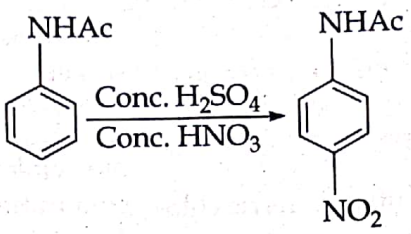
$$RCONH_2 + NaOH \rightarrow RCOONa + NH_3$$
$$RCOONa + HCl \rightarrow RCOOH$$

■ **Bromo derivative (Suitable for Anilido group) :** 1 g of the sample is dissolved in 8-10 ml of glacial acetic acid (heating may be required to hasten the process of dissolution) in a 100 ml beaker. A solution of 0.8 g of potassium bromate and 2.8 g of potassium bromide in 10 ml of water is added slowly to the acetic acid solution of the sample kept in the beaker. The mixture is kept for 5 minutes at room temperature. Then 5 ml of (1:1) hydrochloric acid is added and the reaction mixture is kept at room temperature for 20 minutes. Contents of the beaker is then poured into crushed ice and stirred well with a glass rod. The solid product is filtered off, washed thoroughly with cold water and recrystallised from aqueous ethanol.



■ **Nitro derivative (Suitable for Anilido group) :** 1 g of the sample is dissolved in 5 ml of glacial acetic acid (heating may be required to hasten the process of dissolution) in a test tube. Then 2 ml of conc. sulphuric acid is added to it and the whole content is cooled in an ice-bath. A mixture of 1 ml of conc. sulphuric acid and 1 ml of conc. nitric acid is taken in another test tube. When the previous mixture is sufficiently cooled, the mixed acid is added to it drop by drop with occasional shaking. The test tube is allowed to stand at room temperature for 10 minutes

and then it is poured into crushed ice with stirring. The solid product is filtered off, washed thoroughly with cold water and recrystallised from aqueous ethanol.



5.1.6 Reporting of Unknown Organic Sample

[Some representative examples are given in order to make the students familiar with the pattern of reporting of an unknown organic sample]

Sample No. 1

① **Preliminery Investigation :**

a. Colour :Golden yellow
b. Texture : Crystalline solid
c. Odour : No characteristic smell

② Melting point of the compound = 114°C

③ **Solubility test :**

Water	Dilute HCl	Dilute NaOH	Saturated $NaHCO_3$ solution
×	✓	×	×

As the sample is soluble in dilute HCl it may contain basic functional group like $-NH_2$.

④ **Detection of special elements [Lassaigene's test] :**

A small amount of the sample is strongly fused with a pea sized sodium in a fusion tube until the bottom of the tube becomes red hot. The tube is then broken with a pestle into ~ 10 ml of distilled water contained in a mortar. The mixture is ground thoroughly with the pestle. The mixture is then filtered. The filtrate, known as sodium extract, is used for the following tests.

Experiment	Observation	Inference
1. *Test for Nitrogen* A little of the filtrate is boiled with a pinch of solid ferrous sulphate, cooled and acidified with 6(N) sulphuric acid.	Deep blue colouration.	N present
2. *Test for Halogen* A little of the filtrate is boiled with conc. Nitric acid. The solution is cooled and treated with a few drops of silver nitrate solution.	No precipitate	Halogen (Cl, Br, I) absent
3. *Test for Sulphur* A few drops of sodium nitroprusside solution is added to a small portion of the filtrate.	No violet or purple colouration	S absent

⑤ **Detection of functional groups :**

Experiment	Observation	Inference
1. ***Test for* —COOH *group :*** A pinch of the given sample is added to a saturated solution of $NaHCO_3$.	No effervescence observed.	—COOH absent
2. ***Test for phenolic* —OH *group :*** A few drops of freshly prepared solution of ferric chloride is added to an ethanolic solution of the sample.	No violet or green colouration	Phenolic-OH absent
3. ***Test for carbonyl group :*** 2,4-D.N.P. solution is added to an ethanolic solution of the sample.	No Yellow or orange precipitate	Carbonyl group absent
4. ***Test for olefinic unsaturation :*** A few drops of very dilute potassium permanganate solution is added to an ethanolic solution of the sample.	Pink colour of permanganate disappears	Olefinic unsaturation or easily oxidisable group present
5. ***Test for aromatic* —NH_2 *group :*** The given sample is dissolved in excess of dilute hydrochloric acid. The solution is cooled in ice and a cold, saturated solution of sodium nitrite is added to it. The resulting solution is then added to an ice-cold, alkaline solution of β-naphthol.	Brilliant red dye is formed	Aromatic —NH_2 group present
6. ***Test for aromatic* —NO_2 *group :*** An aqueous ethanolic solution of the given sample is boiled with zinc dust and solid ammonium chloride. The mixture is cooled and filtered into Tollen's reagent.	Black precipitate	—NO_2 group present
7. ***Test for* —$CONH_2$ *or Imide group :*** The given sample is heated with 2-3 beads of solid sodium hydroxide.	No smell of ammonia perceived	Amide —$CONH_2$ or imide $\{CONHCO\}$ group absent
8. ***Test for* —CONHAr *(anilido)group :*** As aromatic —NH_2 group is present test for anilido group is not performed.		

⑥ **Literature Survey :**

From .....(Title of the book) by.....(author name)

Special Element present	Functional group present	Observed Melting Point	Compound(s) in the literature melting point within ± 10 °C	Possible derivative(s) with melting point
Nitrogen (N)	1. Aromatic —NH_2 2. Aromatic —NO_2	114°C	1. 2-Methyl-5-nitroaniline (107°C) 2. *m*-Nitroaniline (114°C) 3. 4-Methyl-2-nitroaniline (117°C) 4. 2,4-Dimethyl-5-nitroaniline (123°C)	1. Acetyl ((151°C) Benzoyl (183°C) 2. Acetyl ((155°C) Benzoyl (155°C) 3. Acetyl ((96°C) Benzoyl (148°C) 4. Acetyl ((159°C) Benzoyl (200°C)

⑦ **Preparation of Derivatives of the Given Sample :**

(a) Preparation of Acetyl Derivative

About 1 g of the given sample is dissolved in minimum volume of acetone in a dry test tube, cooled in an ice bath andto it 1 ml of pyridine is added. ~ 1ml of acetyl chloride is added slowly to the amine solution with stirring. The reaction mixture is heated on a water bath for 10 minutes. The whole content of the test tube is then poured into crushed ice and stirred well with a glass rod.

The precipitated product is filtered off, washed thoroughly with cold water and recrystallised from aqueous ethanol.

Melting point of the recrystallised acetyl derivative of the given sample is 154°C.

(b) Preparation of Benzoyl Derivative

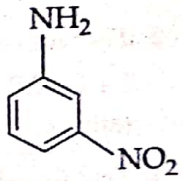
About 0.5 g of the given sample is dissolved in minimum volume of acetone in a 100 ml dry conical flask.10 ml of 10% sodium hydroxide solution is added to it. About 1-1.5 ml of benzoyl chloride is added slowly with constant stirring to the alkaline solution of the sample. The flask is corked tightly and shaken vigorously with occasional cooling in an ice- cold water bath. Shaking is continued till the disappearance of the odour of benzoyl chloride.

The precipitated product is filtered off, washed thoroughly with water and recrystallised from aqueous ethanol.

Melting point of the recrystallised benzoyl derivative of the given sample is 152°C.

⑧ **Conclusion :**

Comparing the melting points of the acetyl and benzoyl derivatives with respective literature values, it could be confirmed that the given sample (with melting point = 114°C) having Nitrogen as special element, aromatic NH_2 and aromatic NO_2 as functional groups is *m*-nitroaniline.



Sample No. 2

① **Preliminary Investigation :**

a. Colour : White

b. Texture : Amorphous

c. Odour : No characteristic smell

② **Melting point of the compound = 138°C**

③ **Solubility test :**

Water	Dilute HCl	Dilute NaOH	Saturated $NaHCO_3$ solution
×	×	✓	×

As the sample is soluble in dilute NaOH solution, but insoluble in $NaHCO_3$ solution, weakly acidic functional group like phenolic —OH and or imide may be present.

④ **Detection of special elements [Lassaigene's test] :**

A small amount of the sample is strongly fused with a pea sized sodium in a fusion tube until the bottom of the tube becomes red hot. The tube is then broken with a pestle into ~ 10 ml of distilled water contained in a mortar. The mixture is ground thoroughly with the pestle. The

mixture is then filtered. The filtrate, known as sodium extract, is used for the following tests.

Experiment	Observation	Inference
1. *Test for Nitrogen* A little of the filtrate is boiled with a pinch of solid ferrous sulphate, cooled and acidified with 6(N) sulphuric acid.	Deep blue colouration.	N present
2. *Test for Halogen* A little of the filtrate is boiled with conc. Nitric acid. The solution is cooled and treated with a few drops of silver nitrate solution.	No precipitate	Halogen (Cl, Br, I) absent
3. *Test for Sulphur* A few drops of sodium nitroprusside solution is added to a small portion of the filtrate.	No violet or purple colouration	S absent

⑤ Detection of functional groups :

Experiment	Observation	Inference
1. *Test for* —COOH *group :* A pinch of the given sample is added to a saturated solution of $NaHCO_3$.	No effervescence observed.	—COOH absent
2. *Test for phenolic* —OH *group :* A few drops of freshly prepared solution of ferric chloride is added to an aqueous or ethanolic solution of the sample.	violet colouration	Phenolic —OH present
3. *Test for carbonyl group :* 2,4-D.N.P. solution is added to an ethanolic solution of the sample.	No Yellow or orange precipitate	Carbonyl group absent
4. *Test for olefinic unsaturation :* A few drops of very dilute potassium permanganate solution is added to an ethanolic solution of the sample.	Pink colour of permanganate disappears	Olefinic unsaturation or easily oxidisable group present
5. *Test for aromatic* —NH_2 *group :* The given sample is dissolved in excess of dilute hydrochloric acid. The solution is cooled in ice and a cold, saturated solution of sodium nitrite is added to it. The resulting solution is then added to an ice-cold, alkaline solution of β-naphthol.	No orange or red dye is formed	Aromatic —NH_2 group absent
6. *Test for aromatic* —NO_2 *group :* The given sample is boiled with a granule of tin and concentrated hydrochloric acid. The mixture is diluted with water and ice-cooled. A cold, saturated solution of sodium nitrite is added to this solution. The resulting solution is added to an ice-cold, alkaline solution of β-naphthol.	No brilliant orange or red dye	—NO_2 group absent
7. *Test for* —$CONH_2$ *or Imide group :* The given sample is heated with 2-3 beads of solid sodium hydroxide.	Smell of ammonia perceived	Amide —$CONH_2$ or imide(-CONHCO-) group present

Experiment	Observation	Inference
8. *Test for* —CONHAr *(anilido)group :* The given sample is heated with Concentrated hydrochloric acid. The solution is diluted with water and ice-cooled. A cold, saturated solution of sodium nitrite is added to this solution. The resulting solution is added to an ice-cold, alkaline solution of β-naphthol	No orange or red dye is formed	—CONHAr absent

⑥ **Literature Survey :**

From .....(Title of the book) by.....(author name)

Special Element present	Functional group present	Observed Melting Point	Compound(s) in the literature melting point within ± 10 °C	Possible derivative(s) with melting point
Nitrogen (N)	Phenolic -OH Easily oxidizable group Amide ($CONH_2$) or Imide $\left(-CONHCO-\right)$	138°C	Salicylamide (139°C)	Hydrolysis product (155°C)

⑦ **Preparation of derivative of the given sample by hydrolysis :**

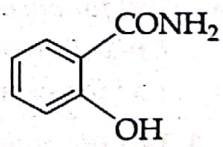
1 g of the sample is heated with 25 ml of 20% sodium hydroxide solution in a 100 ml conical flask for 30 minutes until the disappearance of the smell of ammonia. The reaction mixture is cooled and acidified with concentrated hydrochloric acid.

The solid product is filtered off, washed thoroughly with cold water and recrystallised from hot water.

Melting point of the recrystallised product is 154°C.

⑧ **Conclusion :**

Comparing the melting point of the hydrolysed derivative with respective literature value, it could be confirmed that the given sample (with melting point = 138°C) having nitrogen as special element, $-CONH_2$ and phenolic —OH as functional groups is ***Salicylamide***.



Sample No. 3

① **Preliminary Investigation :**

a. Colour : White

b. Texture : Amorphous

c. Odour : characteristic smell

② **Melting point of the compound = 80°C**

③ **Solubility test :**

Water	Dilute HCl	Dilute NaOH	Saturated $NaHCO_3$ solution
×	×	✓	×

As the sample is soluble in dilute NaOH solution, but insoluble in $NaHCO_3$ solution, weakly acidic functional group like phenolic $-OH$ and or imide may be present.

④ **Detection of special elements [Lassaigene's test] :**

A small amount of the sample is strongly fused with a pea sized sodium in a fusion tube until the bottom of the tube becomes red hot. The tube is then broken with a pestle into ~ 10 ml of distilled water contained in a mortar. The mixture is ground thoroughly with the pestle. The mixture is then filtered. The filtrate, known as sodium extract, is used for the following tests.

Experiment	Observation	Inference
1. *Test for Nitrogen* A little of the filtrate is boiled with a pinch of solid ferrous sulphate, cooled and acidified with 6(N) sulphuric acid.	No blue colouration or Precipitate.	N absent
2. *Test for Halogen* A little of the filtrate is boiled with conc. Nitric acid. The solution is cooled and treated with a few drops of silver nitrate solution.	No precipitate	Halogen (Cl, Br, I) absent
3. *Test for Sulphur* A few drops of sodium nitroprusside solution is added to a small portion of the filtrate.	No violet or purple colouration	S absent

⑤ **Detection of functional groups :**

Experiment	Observation	Inference
1. *Test for* **$-COOH$** *group :* A pinch of the given sample is added to a saturated solution of $NaHCO_3$.	No effervescence observed.	$-COOH$ absent
2. *Test for phenolic* **$-OH$** *group :* A few drops of freshly prepared solution of ferric chloride is added to an ethanolic solution of the sample.	violet colouration	Phenolic-OH present
3. *Test for carbonyl group :* 2,4-D.N.P. solution is added to an ethanolic solution of the sample.	Orange precipitate	Carbonyl group present
4. *Test for* **$-CHO$** *group :* An ethanolic solution of the sample is added to Tollen's reagent and the test tube is heated on a water bath for ~5 minutes.	Black precipitate	$-CHO$ or α-hydroxy keto group present
5. *Test for olefinic unsaturation :* A few drops of very dilute potassium permanganate solution is added to an ethanolic solution of the sample.	Pink colour of permanganate disappears	Olefinic unsaturation or easily oxidisable group present

As nitrogen is absent in the given sample, therefore tests for nitrogenous functional groups i.e. Aromatic $-NH_2$, Aromatic $-NO_2$, Amide ($-CONH_2$), Imide $+CONHCO+$ and Anilide ($-CONHAr$) are not performed.

⑥ **Literature Survey :**

From .....(Title of the book) by.....(author name)

Special Element present	Functional group present	Observed Melting Point	Compound(s) in the literature melting point within ± 10 °C	Possible derivative(s) with melting point
Nil	Phenolic —OH Aldehyde (—CHO) Easily oxidizable group	80°C	Vanillin (81°C)	2,4-DNP (271°C) Oxime (117°C)

⑦ **Preparation of derivatives of the given sample :**

(a) Preparation of 2,4-DNP derivative :

In a test tube, 0.5 g of the given sample dissolved in minimum volume of ethanol. 0.25 g of 2,4-dinitro phenyl hydrazine hydrochloride is added to 5 ml of methanol and stirred well with a glass rod. 1 ml of conc. sulphuric acid is added to it. This solution is added to the sample solution and the mixture is shaken thoroughly.

The precipitated product is filtered off, washed thoroughly with ethanol and recrystallised from absolute alcohol.

Melting point of the recrystallised product is >200°C.

(b) Preparation of oxime derivative :

~ 2 g of hydrated sodium acetate and 1 g of hydroxylamine hydrochloride are dissolved in 5 ml of water. 1 g of the sample is dissolved in minimum volume of ethanol and the ethanolic solution is added to the aqueous solution of hydroxylamine hydrochloride and sodium acetate. The mixture is shaken vigorously and allowed to stand for 10 minutes.

The precipitated product is filtered off, washed thoroughly with cold water and recrystallised from aqueous ethanol.

Melting point of the recrystallised product is 114°C.

⑧ **Conclusion :**

Comparing the melting points of the 2,4-DNP and oxime derivatives with respective literature values, it could be confirmed that the given sample (with melting point = 80°C) having no special element, phenolic —OH and aldehydeas functional groups is Vanillin.