2. **Elemental Analysis**

N, S, Cl, Br, I None

3. **i) Solubility test**

H_2O	5% NaOH	5% $NaHCO_3$	5% HCl	Conc. H_2SO_4	Expected Class
–	soluble	soluble	–	–	Acidic phenols, carboxylic acids

iii) Reaction to pH paper neutral

4. **Physical Constants**

Melting point observed 122 - 124°C

5. **Class determination**

i) with aq. $FeCl_3$ no colour
ii) with alcoholic $FeCl_3$ green solution

Comment: These tests indicate the presence of phenolic compound.

6. **Examination of literature**

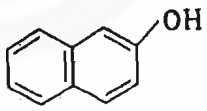
Possible compound	M.P.	Derivatives Benzoate	1-Naphthyl Urethane
2-Naphthol	123°C	107°C	157°C

Comments: Picric acid also have M.P. 122°C. Elemental analysis shows negative test for nitrogen element. That's why it is not selected.

7. **Preparation of derivatives**

(a) Derivative chosen Benzoate
M.P. observed 106 - 107°C
M.P. in literature 107°C
(b) Derivative chosen 1-Naphthyl urethane
M.P. observed 156-158°C
M.P. in literature 157°C

8. The unknown compound is 2-naphthol. The structure of this compound is



UNIT 4 QUALITATIVE CLASSIFICATION TESTS AND PREPARATION OF DERIVATIVES–I

Structure

4.1 INTRODUCTION

In the last Unit you have studied elementary analysis methods of organic compounds, e.g., physical examination, elemental analysis, solubility test and determination of physical constants etc. In this unit first you will learn the identification of organic compounds having carbon, hydrogen and oxygen elements (aldehydes, ketones, alcohols, phenols, carboxylic acids and esters) and then you will study the methods for the preparation of their derivatives.

Objectives

After studying this unit, you should able to test and derivatise the following compounds :

- Aldehydes and Ketones
- Alcohols
- Phenols
- Carboxylic acids
- Esters

4.2 FUNCTIONAL GROUP IDENTIFICATION

Organic compounds are classified into different classes based on the presence of functional groups. Except in the teaching laboratory, it is rare for an unknown compound to possess just one functional group. You must always be aware of the possibility that more than one functional group may be present. However, here we will examine only monofunctional compounds.

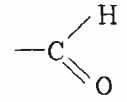
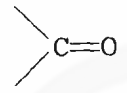
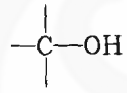
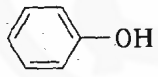
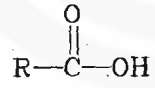
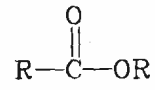
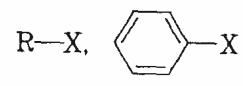
You can recall from your theory course that the functional groups are the sites of chemical reactions. The determination of functional groups depends on their specific features of structure and reactivity. The identification of functional group depends basically on the correct determination of the elements. Common monofunctional organic compounds are

listed in Table 4.1. For our convenience, in this unit, we arrange the organic compound on the basis of elements present in the compound.

From the experimental result so far (elemental analysis, M.P., B.P., solubility test etc.), you will have some idea about the type of functional groups present in your unknown compound. Firstly, it is necessary to confirm the presence of these expected functional groups through classical method. In the next step prepare at least one crystalline derivative to identify actual compound by comparing their melting point with the literature value. Melting points and/or boiling points of some common organic compounds and their derivatives are given at the end of this block (see Appendix).

As said earlier, solid substance prepared from the compound is known as its derivative. In general, the basic structure of the original substance is retained in the derivative. The choice for the preparation of derivative is largely based on the functional group. The ideal derivative should be simply and quickly prepared in high yield and should be easily purified. The derivatives prepared should have sharp and definite melting point. The melting point of the selected derivative should be sufficiently different from that of the same derivative of other compound of a particular organic class.

Table 4.1 : Common monofunctional organic compounds

Functional Group	Class	Nature
A) When C, H and O are present		
1) 	Aldehydes	Neutral
	Ketones	Neutral
2) 	Alcohols	Neutral
3) 	Phenols	Weakly acidic
4) 	Carboxylic acids	Acidic
5) 	Esters	Neutral
B) When C and H are present		
6) 	Alkenes	Neutral
7) 	Alkynes	Neutral
8) Ar–R	Arenes	Neutral
C) When C, H and X are present		
9) 	Halides	Neutral
D) When C, H, N presnet		
10) RR'R"N	Amines	Basic
E) When C, H, N and O present		
11) $-NO_2$	Nitro Compounds	Neutral
12) $-CONH_2$	Amides	Neutral

Now let us discuss each functional group test individuality.

4.3 ALDEHYDES (R–C–H) AND KETONES (R–C–R')

Both aldehydes and ketones have carbonyl group (>C=O). You have studied the reactions of carbonyl group in organic chemistry course (CHE–05). In this unit you will study the tests for detecting aldehydes and ketones.

4.3.1 Functional Group Test

A) Brady's Test

The carbonyl compounds (aldehydes/ketones) react with 2, 4–dinitrophenylhydrazine (DNP) and give crystalline 2, 4–dinitrophenylhydrazone product with orange/yellow/red colour. This test is carried out as given below :

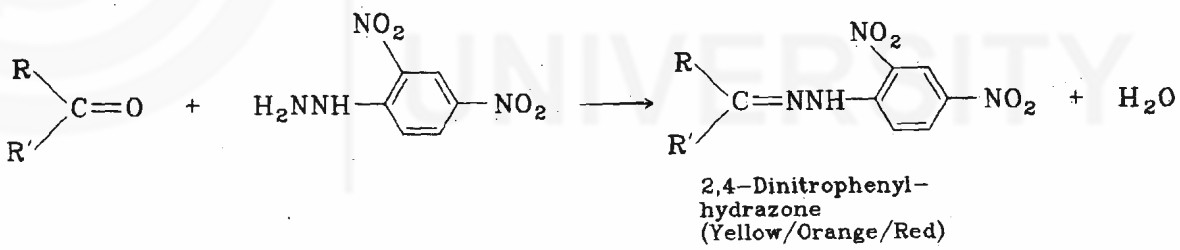
Procedure

Take 0.5 g of the unknown compound in a test tube and dissolve it in few drops of water or ethanol. Add 1 cm^3 of Brady's reagent. Heat the reaction mixture on water bath for few minutes and then cool it in ice. The appearance of yellow/orange/red crystalline precipitate (ppt) indicates the presence of aldehydes or ketones.

The colour of the precipitate gives some idea of the type of carbonyl compounds.

Colour of Precipitate	Compound
Yellow	Saturated carbonyl compounds
Orange	α, β–Unsaturated carbonyl compounds
Red	Aromatic carbonyl compounds

The reaction involves in the Brady's test is given :



2,4–Dinitrophenyl–hydrazone (Yellow/Orange/Red)

Brady's reagent : Dissolve 1 g of DNP in 5 cm^3 concentrated sulphuric acid. Add this solution slowly with shaking and cooling to a mixture of water (7 cm^3) and ethanol (25 cm^3). Filter it to remove any suspended solid and store as a stock solution.

B) Tollen's Test

If Brady's test is positive, than aldehydes and ketones are differentiated through Tollen's test. A positive Tollen's test indicates the presence of an aldehyde. Normally, ketones do not give Tollen's test but there are few exceptions, for example acetophenone and cyclohexanone. Some easily oxidisable compounds (e.g., certain phenols, 2–naphthol; and amines) also give positive Tollen's test but these compounds do not give positive test with DNP.

Silver ammonium ion $[Ag(NH_3)_2]^+$ is present in Tollen's reagent. In this test aldehyde is oxidised to carboxylic acid and silver ion reduced to free silver.

Procedure

Place unknown compounds (2 drops of liquid or 0.05 g of solid) and 1 cm^3 of freshly prepared Tollen's reagent in a cleaned test tube. Shake the test tube and place it in the

stand for about 10 minutes. If black precipitate or silver mirror on the wall of test tube is not appeared, warm the test tube for few minutes on a water bath. Formation of black precipitate or silver mirror indicates the presence of aldehydic group.

The reaction can be given as :

$$RCHO + 2Ag(NH_3)_2OH \longrightarrow 2Ag\downarrow + RCOO\,NH_4 + 3\,NH_3 + H_2O$$

Tollen's reagent (colourless) — Silver mirror or Black ppt.

Tollen's reagent:

Solution A: Dissolve silver nitrate (2.5 g) in distilled water (40 cm^3).

Solution B: Dissolve potassium hydroxide (3 g) in distilled water (40 cm^3).

Mix equal volumes of solution A and B. A white precipitate (Ag_2O) is obtained. Now add concentrated ammonia solution (30%) drop by drop until the mixture is almost clear.

$$Ag_2O + 4NH_3 + H_2O \longrightarrow 2[Ag(NH_3)_2]^+OH$$

Tollen's reagent should be prepared immediately before the experiment because on long standing it decomposes to yield a potentially explosive solid, silver nitride (Ag_3N).

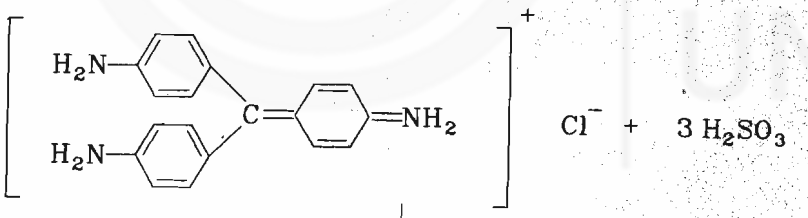
C) Schiff Test

Another method for distinguishing between aldehyde and ketone is Schiff Test. Aldehydes give positive Schiff's test whereas ketones do not react with Schiff's reagent. In this test an aldehyde reacts with Schiff's reagent to form a characteristic magenta colour. Some aromatic aldehydes (e.g., vanilin), give a negative result with the Schiff's reagent. Methyl ketones (CH_3CO–) may restore the colour of Schiff's reagent very slowly. Your test tube should be free from alkali and the salts of weak acids because these also redden the Schiff's reagent like an aldehyde. Perform this test as given below:

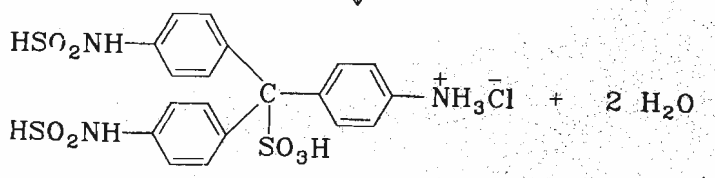
Procedure

Place 2 cm^3 of unknown compound or 2 cm^3 of aqueous or alcoholic solution of the unknown compound in a test tube. Then add 2 cm^3 of Schiff's reagent in the test tube and shake it for 2 minutes. **Do not warm or heat** the Schiff's reagent because pink colour develops on heating even in the absence of aldehyde. The appearance of wine–red or purple colour indicates the presence of an aldehyde group.

The reaction sequence of this is:



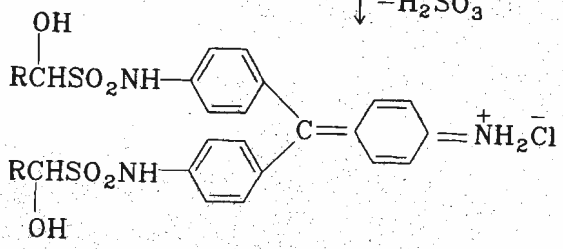
Cl^- + 3 H_2SO_3



+ 2 H_2O

Schiff's reagent (colourless)

2 RCHO
$-H_2SO_3$



Schiff's reagent tends to acquire colour on storage. Therefore, it is necessary to use only colourless Schiff's reagent.

Keep the Schiff's reagent in a well stopped bottle in dark.

Schiff's reagent

Dissolve *p*–rosaniline hydrochloride (0.2g) in saturated solution (20 cm^3) of sulphur dioxide in water. Shake and allow it to stand for few hours until it becomes colourless or pale yellow. Dilute with water (180 cm^3) and separate the clear solution by filtration.

D) Iodoform Test

Iodoform test is useful for the identification of methyl ketones (CH_3COR) and secondary methyl carbinols $CH_3CH(OH)R$. Since this test is positive for $CH_3CH(OH)$– groupings, it is advised that you should perform iodoform test after confirming the presence of carbonyl group. Ethanol, acetaldehyde (ethanal), CH_2ICO– and CHI_2CO– also give positive iodoform test. The test is negative for acetic acid and some other similar compounds. Carry out the test as under.

Procedure

Dissolve 0.5 cm^3 of the unknown liquid or 0.2 g of the solid in water (3 cm^3) or aqueous dioxane (2 cm^3 water + 2 cm^3 dioxane) in a boiling tube. Add iodine–potassium iodide solution (1 cm^3) and then few drops of 3 *M* sodium hydroxide solution with shaking until the brown colouration vanishes. A positive test is indicated by immediate formation of pale yellow precipitate of iodomethane (iodoform), M.P. 119°C, without heating. Reaction involves in the test is given by,

$$CH_3COR \xrightarrow[H_2O]{I_2,\ NaOH} RCO_2Na + \underset{\text{Pale Yellow ppt}}{CH_3I\downarrow}$$

Iodine–potassium iodide reagent: It is prepared by adding 50 g of potassium iodide and 25 g of iodine to distilled water (200 ml). A clear solution is obtained after stirring. Deep brown colour of the solution is due to the formation of triodide anion (I_3)

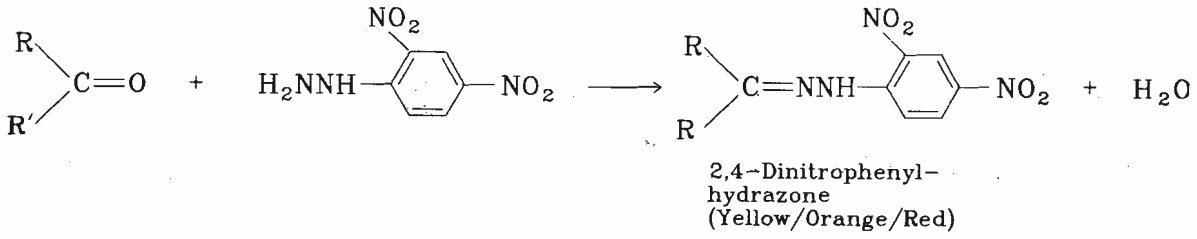
$$KI + I_2 \xrightarrow{H_2O} KI_3$$

4.3.2 Characteristic Derivatives

For the preparation of derivatives, carbonyl group of aldehydes and ketones are converted into another groups such as >C=NNHR, oximes, etc. Methods for the preparation of some common derivatives are given in this section.

1) 2,4–Dinitrophenylhydrazone

Dissolve 0.5 g of the unknown carbonyl compound in a small volume of ethanol and add 2–3 cm^3 of the 2,4–dinitrophenylhydrazine reagent. Heat the mixture on water bath for 15–20 minutes, if no solid separates immediately, cool it and if a precipitate still does not form, add water dropwise untill precipitate forms. Filter off the resulting solid, wash it with aqueous methanol (equal volumes of H_2O) and CH_3OH) and recrystallize the solid from ethanol or ethyl acetate. Take the melting point.

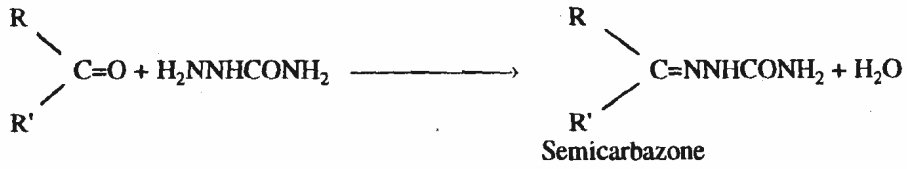


2,4–Dinitrophenyl–hydrazone (Yellow/Orange/Red)

2) Semicarbazone

Dissolve the semicarbozide hydrochloride (0.5g) and sodium acetate (0.8g) in 5 cm^3 of water in a test tube and then add the carbonyl compound (0.5 g). Add minimum amount of ethanol dropwise to get a clear solution if the solution is not clear. Heat the mixture for

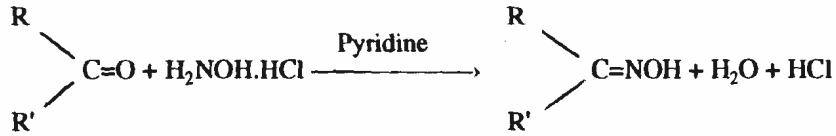
10–20 minutes on a boiling water bath, cool in ice and filter. Recrystallize the product from ethanol, aqueous ethanol, water or benzene.



Semicarbazone

3) Oximes : Derivatives for higher molecular weight Aldehydes and Ketones

Place a mixture of 0.5 g of carbonyl compound, 0.5g of hydroxylamine hydrochloride, 3 cm^3 of pyridine and 3 cm^3 of absolute ethanol in a small round bottom flask. Fit reflux condensor on round bottom flask and reflux the mixture for 2 hrs. on water bath. Evaporate the solvent and recrystallized the residue from ethanol or aqueous ethanol.



Hydroxyl amine hydrochloride

Oxime

SAQ 1

Which of the following compounds will give a positive haloform test ?

(a) $C_6H_5COCH_3$; (b) CH_3COOH; (c) CH_3CHO;

(d) CH_2ICOR; (e) CH_3COCH_2COOR

4.4 ALCOHOLS (R–OH)

You may have studied variety of reactions of alcohols in your theory course. In last section we have seen that alcohols containing $CH_3CH(OH)$ —group give positive iodoform test. In this section we shall study tests for other alcohols.

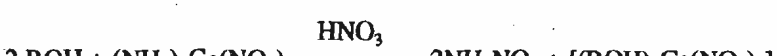
4.4.1 Functional Group Test

A) Ceric Ammonium Nitrate Test

This reagent gives positive test for primary, secondary and tertiary alcohols having upto ten carbon atoms. You carry out the test at room temperature because hot solutions of the reagent oxidizes many of organic compounds.

Procedure

Prepare the solution of the unknown compound (0.2 g or 1 cm^3) in water, (or dioxane for water insoluble compounds) add few drops of ceric ammonium nitrate. A red colour is obtained. This indicates the presence of primary, secondary and tertiary alcohols. Alcohols replace nitrate ions in complex cerate anions, resulting in a change from a yellow to red solution. The preliminary reaction for alcohols is,



Ceric ammonium Nitrate

Red Complex

B) Acetyl Chloride Test

Acetyl chloride reacts vigorously with alcohols to furnish an ester and hydrogen chloride. Compounds, such as carboxylic acids, phenols and amines, also react with this reagent. You should ignore these compounds due to their non–neutrality.

Procedure

In a dry test tube take 0.5 cm^3 of liquid or 0.5 g of solid unknown compound and add 2–3 drops acetyle chloride. Reaction mixture become warm with the evolution of hydrogen

chloride. Bring a rod dipped in ammonium hydroxide near the mouth of test tube. A white fumes indicates the presence of alcohol. Reactions involved in this test is given by,

$$ROH + \underset{\text{Acetyl chloride}}{CH_3COCl} \longrightarrow \underset{\text{Ester}}{ROCOCH_3} + HCl$$

$$HCl + \underset{\text{Ammonium hydroxide}}{NH_4OH} \longrightarrow \underset{\text{White fumes}}{NH_4Cl} + H_2O$$

When test (A) and (B) gives positive results, then perform Lucas test for the identification of primary, secondary and tertiary alcohols.

C) Lucas' Test : Differentiation between Primary, Secondary and Tertiary Alcohols

This test is useful for distinguishing among lower molecular weight primary, secondary and tertiary alcohols. In this reaction alcohols convert to corresponding alkyl chloride. Lucas' test based upon the difference in reactivity of these three classes towards HCl. With Lucas reagent primary alcohols give no appreciable reaction, secondary alcohols react more rapidly and tertiary alcohol react very rapidly.

This test has its limitation. For example allyl alcohols give similar results to that of secondary alcohols. Thus preparation of its derivatives is necessary to confirm the nature of alcohols. Carry out the test as given below :

Procedure

Add Lucas's reagent (3 cm^3) into the unknown compound (0.5 cm^3) in a test tube. Cork the test tube, shake well and then allow the mixture to stand. Note the following observations:

i) Immediately cloud formation indicates the presence of tertiary alcohol.

$$R_3COH + HCl \xrightarrow{ZnCl_2} R_3CCl + H_2O$$

ii) Gradually cloud formation (5–10 minutes) indicates the presence of secondary alcohol.

$$R_2CHOH + HCl \xrightarrow{ZnCl_2} R_2CHCl + HCl$$

iii) No cloud formation indicates the presence of primary alcohol.

$$RCH_2OH + HCl \xrightarrow{ZnCl_2} \text{No reaction.}$$

Lucas' reagent

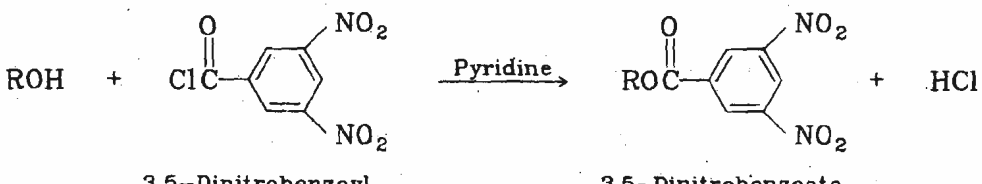
Dissolve anhydrous zinc chloride (35 g) in concentrated hydrochloric acid (25 cm^3) with cooling to avoid loss of hydrogen chloride.

4.4.2 Characteristic Derivatives

Methods for the preparation of some important derivatives of alcohols are given below.

1) 3,5–Dinitrobenzoate Derivatives

The reaction between 3,5–dinitrobenzoyl chloride and alcohol gives the corresponding ester (3,5–dinitrobenzoate). 3,5–Dinitrobenzoate esters are suitable derivatives for both alcohols and phenols. The reaction involves in this preparation is as under:



3,5–Dinitrobenzoyl chloride

3,5–Dinitrobenzoate

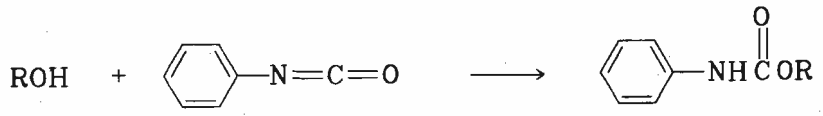
Procedure

Dissolve the alcohol (2 cm^3) in dry pyridine (5 cm^3) and add 3,5–dinitrobenzoyl chloride (1.2 g) in a 100 cm^3 round–bottomed flask. Reflex the reaction mixture for about 30 minutes and pour it into 40 cm^3 of hydrochloric acid. Separate the solid or oily product and stir with 15 cm^3 sodium carbonate solution (1 *M*) to remove any 3,5–dinitrobenzoic acid formed. Filter the solid and recrystallize from petroleum (60–80°C), ethanol or aqueous ethanol.

3,5–Dinitrobenzoyl chloride is reactive towards water; it should be used immediately after weighing. Don't exposure to air and keep the bottle tightly closed.

2) 1–Naphthyl Urethane Derivative

This derivative is also suitable for both alcohols and phenols. When aryl substituted isocyanate, ArN=C=O, react with alcohols, it gives a urethane.



Aryl isocyanate Urethane

A major side reaction is that of water with isocynate. To avoid the side reaction, take precautions to ensure that the alcohol is **anhydrous.**

Procedure

Place the alcohol (0.5 g), dry pyridine (1 cm^3) and 1–naphthylurea (0.5 cm^3) in a dry test tube. Shake, the mixture for few minutes. If no precipitate appears warm gently on a water bath for 5 minutes and then cool the mixture in ice. Filter off the solid product. Recrystallize the crude derivative from petroleum ether (40–60°). (Remove 1–naphthylurea by filtration which is insoluble in petroleum).

Isocyanates are toxic. Take normal precautions in handling them.

SAQ 2

Write "T" if true and "F" if false against the following statements.

a) Ceric ammonium nitrate test for secondary alcohol gives red colour. [ ]

b) Reaction of alcohol with acetyl chloride yields an ester and hydrogen chloride. [ ]

c) Acetyl chloride test is useful for distinguishing primary, secondary and tertiary alcohols. [ ]

d) The reaction between substituted alcohol and isocyanate gives corresponding ester. [ ]

4.5 PHENOLS (Ar–OH)

The aromatic compounds in which hydroxyl (OH) group is directly attached to benzene ring are called phenols. In this section we shall study the functional group test of phenols and preparation of their characteristic derivatives.

4.5.1 Functional Group Test

a) Ferric Chloride Test

Most phenol react with ferric chloride to give colour. Some phenols that do not give colour in aqueous or alcoholic solution, but they do so in chloroform, especially after addition of a drop of pyridine. Some phenol do not give colour at all. So a negative test must not be taken as significant without supporting information.

Procedure

Dissolve 0.5 g of the unknown compound in 1–2 cm^3 of water (or a mixture of water and 95% ethanol if the compound is not water soluble) and add few drops of very dilute (1%) ferric chloride solution. Wide range of colour (given below) shows the presence of phenolic –OH.

OH
|
Enols (R'C=CHR') also give a wide range of colour with $FeCl_3$.

The phenol complexes are probably coordination compounds in which iron is hexavalent.

$$6Ar\text{–}OH \xrightarrow{FeCl_3} [ArO)_6Fe]^{-3} + 6H^+ + 3Cl^-$$

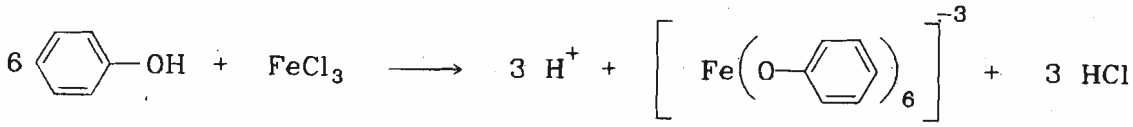
Compound	Colour
Phenol, *o*–Cresol	Violet
p–Cresol, quinol	Blue
m–Cresol, 1–Naphthol(alcoholic)	Blue–violet
Resorcinol	
1–Naphthol	Pink
2–Naphthol (alcoholic)	Green

Following compounds do not respond with ferric chloride,

i) Picric acid

ii) Naphthol sulphonic acid

The reaction involved in this test is,



B) Liebermann's Test

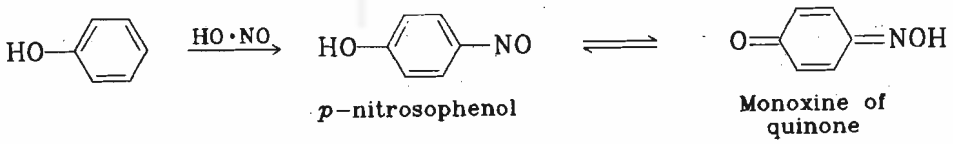
Phenols in which *para* position is free, give positive Liebermann's test. Although few exceptions are noted. For example, *p*–substituted phenols and nitrophenols do not respond to Liebermann's test. Dihydroxyphenols, except resorcinol, do not give satisfactory result with this test.

Procedure

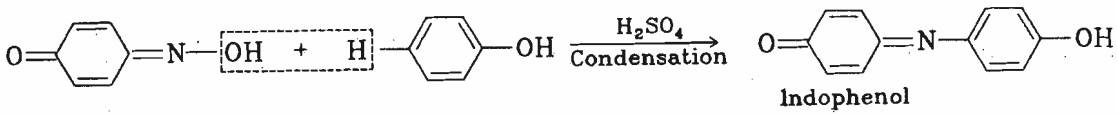
Place few crystals of sodium nitrite and unknown compound (0.5g) in a dry test tube. Heat the mixture gently for about 30 seconds, allow it to cool and add 0.5 cm^3 of conc. sulphuric acid. On shaking the contents a deep green or blue colour develops. Dilute the content with water, the colour changes to red. Now add excess of dilute sodium hydroxide solution, the green or blue colour again reappears. Colour formation is observed due to the production of salt of indophenol. The reactions of the test are:

$$NaNO_2 \xrightarrow{H^+} HNO_2 \longleftrightarrow HO.NO$$

Nitrus acid



p–nitrosophenol — Monoxine of quinone



Indophenol

Green — Blue

C) Ceric Ammonium Nitrate Test

Ceric ammonium nitrate can also be used as a qualitative test for phenols. Experimental procedures for this test is same as discuss in alcohols (4.4.1 A).

4.5.2 Characteristic Derivatives

Many of the derivatives for characterizing alcohols may be used equally successfully for phenols. Some common methods for the preparation of derivatives of phenols are given below.

1) 3,5–Dinitrobenzoate Derivative

Prepare as described under 4.4.2(1)

2) 1-Naphthyl Urethane Derivative

Prepare as described under 4.4.2(2)

SAQ 3

a) Which of the following would give colour with $FeCl_3$

i) *p*–cresol

ii) Phenol

iii) Resorcinol

iv) 2–Napthol (alcoholic)

b) Which one of the following compounds do not respond with $FeCl_3$

i) Picric acid

ii) *o*–cresol

iii) Quinol

iv) 2–Naphthol (alcoholic)

4.6 CARBOXYLIC ACIDS (RCOOH)

Carboxylic acids are represented by general formula RCOOH. The –COOH group is known as carboxylic group. The presence of carboxylic group in the compound is ascertained by following tests:

4.6.1 Functional Group Test

A) Sodium bicarbonate Test

One of the best tests for the carboxylic group is solubility in basic solution. Carboxylic acids liberate carbon dioxide from sodium bicarbonate.

Procedure

Place 0.2 g of the unknown compound in a test tube and add 1 cm^3 of 5% aqueous sodium bicarbonate. Vigorous evolution of carbon dioxide with effervescence indicates the presence of carboxylic group.

$$RCOOH + NaHCO_3 \longrightarrow RCOONa + H_2O + CO_2\uparrow$$

4.6.2 Characteristic Derivatives

Common derivatives for carboxylic acids are: Amides, anilides, *p*–toluidides, phenacyl esters and S–benzylisothiouronium salts. Experimental details for amides, anilides and *p*–toluidides are given below.

Amides, anilides and *p*–tolulidides are prepared from the corresponding acid chloride by treatment with either ammonia, aniline or *p*–toluidine, respectively. It is considered that the method for the preparation of anilides and *p*–toluidides has advantage over amide. This is because amides are more soluble in water and as a result are harder to isolate. The acid chlorides are prepared from the acid or its salt, and thionyl chloride.

$$RCOOH + SOCl_2 \longrightarrow RCOCl + SO_2 + HCl$$

Thionyl chloride — Acid chloride

or

$$RCOONa + SOCl_2 \longrightarrow RCOCl + SO_2 + NaCl$$

Thionyl chloride — Acid chloride

Acid chloride, can be used to make the amide, anilides or *p*–toluidides. Therefore, let us first study the method for preparation of acid chloride.

Preparation of Acid Chloride

Place the carboxylic acid (1 g), thionyl chloride (2cm^3) and dimethylformamide (DMF) (5 drops) in a small round bottom flask, attach a reflux condenser and reflux for about 30 minutes. Precipitate of acid chloride will appear at the bottom of the flask. This mixture, containing acid chloride, can be used to prepare amide, anilide or *p*–toludide derivative as described below:

1) Amide Derivative

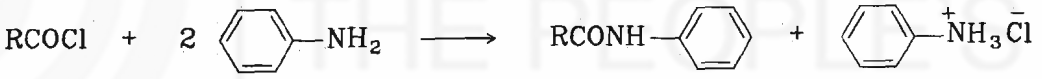
Be very careful while adding conc. NH_4OH, the reaction is quite vigorous.

To 2 gm of the above mixture, containing acid chloride, add 15 cm^3 of ice–cold conc. NH_4OH. A vigorous reaction take place. Filter off the solid formed as the result of the reaction and recrystallize from water or aqueous ethanol.

$$RCOCl + NH_4OH \xrightarrow{\text{cold}} RCONH_2$$

2) *p*–Toluidides and Anilides Derivatives

Take about 2 g of the crude acid chloride in a 100 cm^3 conical flask and dissolved it in 5 cm^3 of acetone. To this add 1 g *p*–toluidine (dissolved in acetone). Shake the mixture for few minutes and add 50 cm^3 of NaOH to the flask. Filter off the solid *p*–toluidide which formed during the reaction. Wash the *p*–toluidide with water and recrystallised from ethanol.



If you want to prepare anilide, use aniline in place of *p*–toluidine and you will get anilides.

SAQ 4

Fill in the blanks.

a) Carboxylic acid liberate.....from sodium bicarbonate.

b) Reaction of acid chloride with ammonia yields.....

c) Reaction of carboxylic acid with .....yields anilides.

4.7 ESTERS $R\overset{O}{\overset{\|}{C}}OOR'$

The product of the reaction between an organic acid and an alcohol is called an ester. They are represented by the general formula:

A number of esters have characteristic odour. Pleasant odours of many fruits and flowers are due to the presence of esters. Some naturally occurring esters and their odours are given in below:

Some esters and their odours

Name	Pentyl acetate	Octyl acetate	Methyl butyrate	Ethyl trityrate
Odour	Bananas	Oranges	Apples	Pineapples

4.7.1 Functional Group Test

A) Hydroxamic Acid Test

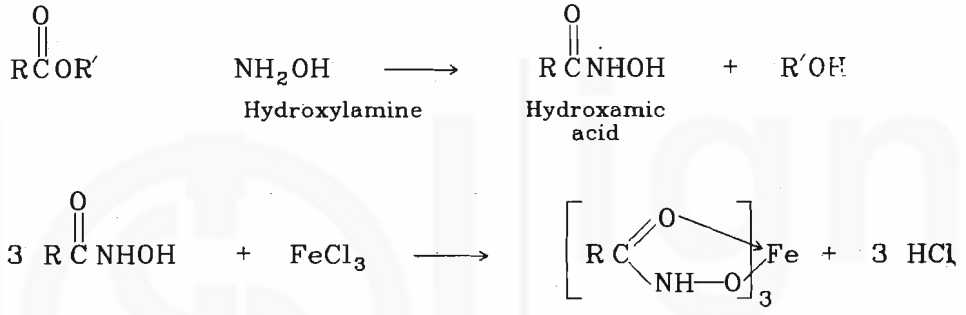
A neutral compound, containing C,H,O, may be an ester or acid anhydride when it does not respond to DNP test for aldehydes and ketones.

Esters react with hydroxylamine to give hydroxamic acid, which then complexes with Fe(III) (ferric chloride) to give a purple or deep red colour. Carboxylic acids anhydrides, acyl halides and phenolic or enolic compounds may interfere with this test. But these compounds can be ruled out by their solubility in aqueous sodium hydroxide.

Procedure

Take 2–3 drop or 0.02 g of unknown compound in a boiling tube and add 0.2 g of solid hydroxylamine hydrochloride and 5 cm^3 10% NaOH solution. Heat the mixture on a boiling water bath. Cool and acidify the reaction mixture with dilute hydrochloric acid and add 2–3 drops of 5% aqueous ferric chloride. Purple or deep red colour due to formation of ferric complex of hydroxamic acid indicates the presence of ester.

The chemical reaction of the test is :



B) Hydrolysis Test

Most esters undergo hydrolysis very slowly. Anhydrides are hydrolysed quickly.

Procedure

Dissolve the ester (0.5 g) in ethanol (2 cm^3), add dilute methanolic potassium hydroxide (2–3 drops) and phenolphthalein (2 drops) in a test tube. In another test tube prepare similar mixture but omit the ester. A pink colour is obtained in both the test tube. Now place both test tubes in boiling water for 5 minute. The pink colour fades or disappears in first test solution, whereas in second pink colour remains as such. This indicates the presence of ester group in the supplied sample.

Pink colour disappears when the alkali is used in hydrolysis of ester. Phenolphthalein is colourless in acidic medium and pink in basic medium.

$$RCOOR' \xrightarrow{KOH} RCOOKa + R'OH$$

4.7.2 Characteristic Derivatives

Esters are identified by their amide derivatives and usually by their hydrolysis products (alcoholic and acidic partners).

1) Amide Derivatives

Take about 0.5 g of the ester, 10–15 cm^3 water 4–5 cm^3 concentrated ammonia in a test tube and shake well. Filter off the precipitate of amide, formed during the reaction, wash with water and dry it.

$$RCOOR' \xrightarrow{NH_3} \underset{\text{Amide}}{RCONH_2} + R'OH$$

2) Hydrolysis of Esters and Isolation of Components

The esters on hydrolysis give parent acids and alcohols or phenols. These compounds can be isolated. They serve as derivatives or they are further derivatised.

Place the ester (4 g) and 20% methanolic potassium hydroxide (30 cm^3) in a round bottom flask and reflux the mixture until hydrolysis is complete (generally completion of reaction is indicated by change in appearance of reaction mixture). Allow the round bottom flask to cool and do as follows:

(a) If a solid precipitates

i) filter it off, wash with methanol and characterise it for the acid, or phenol (prepare suitable derivative).

ii) remove the methanol from the filtrate and identify the liquid for alcohols or phenols (prepare derivative).

(b) If homogeneous solution is obtained

Distill the methanol on water bath, cool and extract the residue with diethyl ether. Dry the ether extracts over anhydrous sodium sulphate, evaporate the ether and identify the residue for alcohols. Characterise the ether–insoluble residue for carboxylic acids.

Hydrolysis of an ester is given by,

$$RCOOR' \xrightarrow{KOH} RCOOK + R'OH$$

$$RCOOK \xrightarrow{H^+} RCOOH$$

SAQ 5

Complete the following reactions :

a) $C_2H_5COOCH_3 + KOH \xrightarrow{H^+}$ ..... + ...

b) $CH_3COOCH_3 + NH_2OH \longrightarrow$ ..... + ...

c) $CH_3COOC_2H_5 + NH_3 \longrightarrow$ ..... + ...

4.8 ANSWERS OF SAQs

1) a, c and d

2) a) T; b) T; c) F; d) F

3) a) All four b) i

4) a) Carbon dioxide b) Amide c) Aniline

5) a) $C_2H_5COOH + CH_3OH$

b) $CH_3CONHOH + CH_3OH$

c) $CH_3CONH_2 + C_2H_5OH$