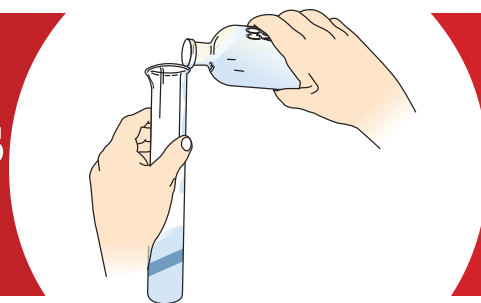


UNIT-8

TESTS FOR FUNCTIONAL GROUPS IN ORGANIC COMPOUNDS



EXPERIMENT 8.1

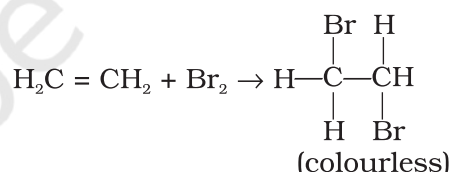
Aim

To identify the functional groups present in an organic compound.

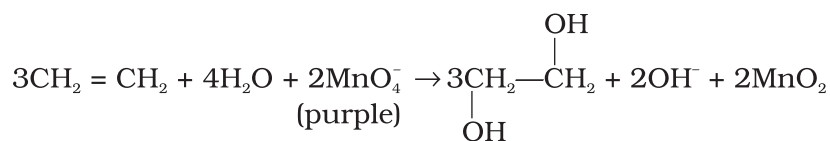
I. TESTS FOR UNSATURATION

Theory

Organic compounds containing $>C=C<$ and / or $-C\equiv C-$ bonds are called unsaturated compounds. These compounds undergo addition reaction with bromine water or the solution of bromine in carbon tetrachloride, chloroform or glacial acetic acid. Addition of bromine to an alkene results in the formation of vicinal dibromide. The reddish orange colour of the solution of bromine in carbon tetrachloride disappears on reaction with an alkene. The reaction is as follows :



Alkenes decolourise the neutral/alkaline KMnO_4 solution and vicinal glycols are formed (**Bayer's test**). Reaction takes place as follows :



Both the above reactions are used as tests for unsaturation.

Material Required



- Test tubes : Two
- Test tube holder : One



- Potassium hydroxide solution : 1–2 mL
- Carbon tetrachloride/ chloroform : 2 mL
- Bromine water/solution of bromine in CCl₄ or chloroform : 2 mL
- Potassium permanganate solution : As per need
- Compound to be tested : As per need

Procedure

A. Bromine water test

Dissolve 0.1 g or 5 drops of organic compound in 2 mL of carbon tetrachloride in a test tube and add 2% solution of bromine in carbon tetrachloride or bromine water drop by drop with continuous shaking. Decolourization of bromine solution indicates the presence of unsaturation in organic compound.

Potassium hydroxide



Carbon tetrachloride



Chloroform



Bromine



Potassium permanganate



B. Bayer's test

Dissolve 25-30 mg of organic compound in 2 mL of water or acetone (free of alcohol) and add 1% potassium permanganate solution containing equal volume of 1% sodium carbonate solution. The discharge of the colour of more than one drop of potassium permanganate indicates the presence of unsaturation in the organic compound. Carrying out the reaction under alkaline conditions removes the possibility of confusion due to substitution in aromatic compounds.

Note: (i) Unsaturation in an organic compound is confirmed only when both of the above tests are positive.

(ii) In place of CCl₄ any other solvent such as CHCl₃/dioxan and even water can be used to dissolve the organic compound for carrying out the reaction.

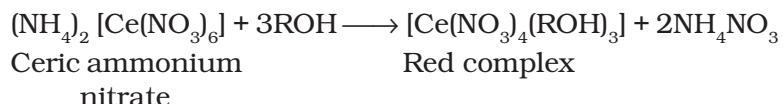
Precautions

- (a) The tests should be performed at room temperature.
- (b) Handle bromine solution carefully. Do not inhale the vapours and also avoid its contact with the skin.

II. TEST FOR ALCOHOLIC (R-OH) GROUP

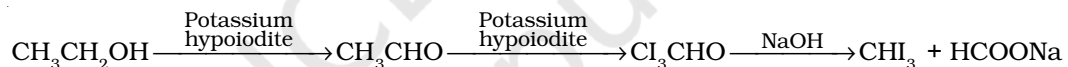
Theory

Alcoholic compounds on reaction with ceric ammonium nitrate give a red colouration due to the formation of a complex.



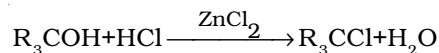
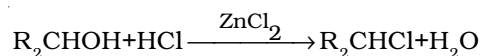
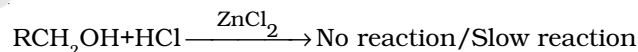
Distinction between primary, secondary and tertiary alcohols can be done on the basis of iodoform test and Lucas test.

Ethanol and secondary alcohols which contain $\text{CH}_3\text{—CH}(\text{OH})\text{R}$ group (iodoform reaction) give positive iodoform test. To carry out reaction, potassium iodide and sodium hypochlorite solution are added to the compound in the presence of sodium hydroxide solution. Probably sodium hypochlorite first oxidises potassium iodide into potassium hypoiodite, which oxidises $\text{CH}_3\text{—CH}(\text{OH})\text{R}$ group to CH_3COR group and then iodinate it in the alkaline medium of the reaction mixture by replacing the α -hydrogen attached to the carbon atom adjacent to carbonyl group by iodine. Iodoform is formed after cleavage of C—C bond.



Lucas Test

Lucas reagent contains zinc chloride and concentrated hydrochloric acid. This reagent reacts with primary, secondary and tertiary alcohols at different rates. Tertiary alcohols react almost instantaneously, secondary alcohols react in about 1-5 minutes and primary alcohols react very slowly. The reaction may take 10 minutes to several days.



Alcohols are soluble in Lucas reagent but the formed alkyl halides are not soluble. Therefore, formation of two layers in the reaction medium indicate the occurrence of the reaction.

- Primary alcohols – Layers do not separate
- Secondary alcohols – Layers separate within 1-5 minutes
- Tertiary alcohols – Layers separate immediately

Material Required



- Test tube holder : One
- Test tubes : As per need



- Ceric ammonium nitrate solution : As per need
- Sodium hydroxide : As per need
- Iodine solution : As per need
- Lucas reagent : As per need
- Dioxan : As per need

Procedure

A. Ceric ammonium nitrate test

Take 1 mL solution of organic compound dissolved in a suitable solvent. Add a few drops of ceric ammonium nitrate solution. Appearance of red colour shows the presence of alcoholic –OH group.

Sodium hydroxide 

Iodine 

Note : The red colour disappears after keeping the reaction mixture for sometime. The colour also disappears if excess of ceric ammonium nitrate solution is added. Therefore, use of excess of ceric ammonium nitrate solution should be avoided.

B. Iodoform test

First method

Take 0.2 mL of the compound in a test tube, add 10 mL of 10% aqueous KI solution and 10 mL of freshly prepared NaOCl solution. Warm gently; yellow crystals of iodoform separate.

Second method

Dissolve 0.1 g or 4 to 5 drops of compound in 2 mL of water. If it does not dissolve, add dioxane drop by drop to get a homogeneous solution. Add 2 mL of 5% sodium hydroxide solution followed by potassium iodide-iodine reagent* dropwise with continuous shaking till a definite dark colour of iodine persists. Allow the reactants to remain at room temperature for 2-3 minutes. If no iodoform separates, warm the reaction mixture in a water bath at 60°C. Add more drops of potassium iodide-iodine reagent. If colour of iodine disappears continue addition of reagent till the colour of iodine persists even after two minutes of heating at 60°C. Remove excess iodine by adding a few drops of sodium hydroxide solution with shaking. Dilute the mixture with equal volume of water and keep it at room temperature for 10-15 minutes. A yellow precipitate of iodoform is obtained if test is positive.

* Potassium iodide-iodine reagent is prepared by dissolving 20 g of potassium iodide and 10 g of iodine in 100 mL of water.

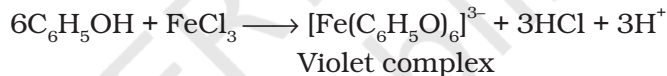
C. Lucas test

Take 1 mL of compound in a test tube. Add 10 mL of Lucas reagent. Shake well and note the time for the separation of two distinct layers.

Note : Lucas test is applicable to only those alcohols which are soluble in the reagent because the test is based on separation of alkyl halides as separate layer.

III. PHENOLIC (AR-OH) GROUP**Theory**

The -OH group attached directly to the ring carbon of an aromatic ring is called phenolic -OH group. Phenols are weakly acidic, therefore they are soluble in NaOH solution but at the same time they are not sufficiently acidic to be soluble in sodium hydrogencarbonate solution. Phenols give coloured complex with neutral ferric chloride solution. For example, phenol gives a complex of violet colour as follows :



Resorcinol, *o*-, *m*- and *p*-cresol give violet or blue colouration, catechol gives green colour which rapidly darkens. 1 and 2-Naphthol do not give characteristics colours. Phenols condense with phthalic anhydride in the presence of concentrated H_2SO_4 , Phenol condenses to give phenolphthalein which gives a dark pink colour with NaOH solution. This is called phthalein dye test.

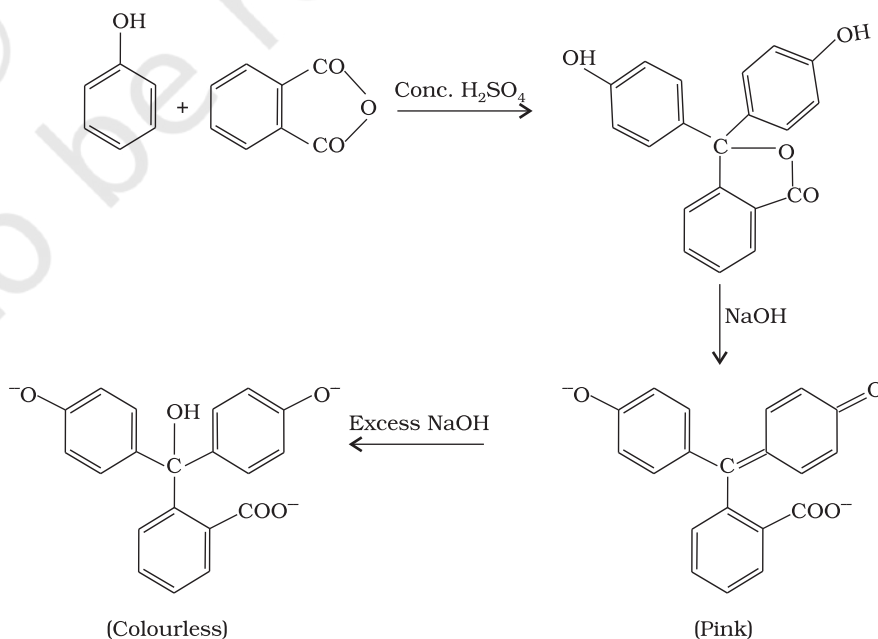




Table 8.1 : Colours produced by some other phenolic compounds in phthalein dye test

Compound	Colour	Compound	Colour
<i>o</i> -Cresol	red	Catechol	Usually blue takes longer time to appear
<i>m</i> -Cresol	bluish-purple	Resorcinol	Green fluorescent colour of fluorescein
<i>p</i> -Cresol	No colour		

Material Required

 <ul style="list-style-type: none"> • Test tube holder : One • Test tubes : As per need 	 <ul style="list-style-type: none"> • Blue litmus paper • Ferric chloride solution • Conc. sulphuric acid • Sodium hydroxide • Phthalic anhydride • Organic compound containing phenolic -OH group 	According to requirement
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Procedure

A. Ferric chloride test

Take 2 mL of aqueous or alcoholic solution of the organic compound in a test tube, add neutral ferric chloride solution dropwise and note the colour change. Appearance of a blue, green, violet or red colour indicates the presence of phenolic -OH group.

Sulphuric acid 

Sodium hydroxide 

Phthalic anhydride 

B. Phthalein dye test

Take 0.1 g of organic compound and 0.1 g of phthalic anhydride in a clean dry test tube and add 1-2 drops of conc. H_2SO_4 . Heat the test tube for about 1 minute in an oil bath. Cool and pour the reaction mixture carefully into a beaker containing 15 mL of dilute sodium hydroxide solution. Appearance of pink, blue, green, red etc. colours indicates the presence of phenolic -OH group in the compound. However, the colour disappears on addition of large excess of sodium hydroxide solution.

Note : (i) Neutral ferric chloride solution is prepared by adding dilute sodium hydroxide solution to ferric chloride solution drop by drop till a small but permanent brown precipitate appears. Solution is filtered and the clear filtrate is used for the test.

(ii) Some phenols like 2,4,6 - trinitrophenol and 2,4 - dinitrophenol, which contain electron withdrawing groups are strong acids and dissolve even in sodium hydrogencarbonate solution.

Precautions

- (a) Always use freshly prepared, neutral and very dilute solution of ferric chloride.
 (b) Phenol is toxic and corrosive in nature and should be handled with care.

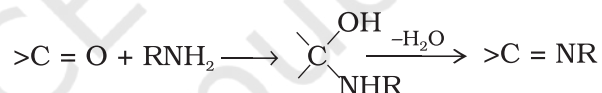
IV. ALDEHYDIC AND KETONIC GROUPS [$-\text{CHO}$ and $-\overset{\text{O}}{\parallel}{\text{C}}-$]

Theory

Both aldehydes and ketones contain carbonyl group ($>\text{C}=\text{O}$) and are commonly known as carbonyl compounds. Identification of aldehydes and ketones is done by two important reactions of carbonyl group i.e.

- (i) addition reaction on double bond of $>\text{C}=\text{O}$ group and
 (ii) oxidation of carbonyl group.

Addition reactions of derivatives of ammonia are important from the point of view of identification of carbonyl compounds. Addition is generally followed by elimination resulting in the formation of unsaturated compound.



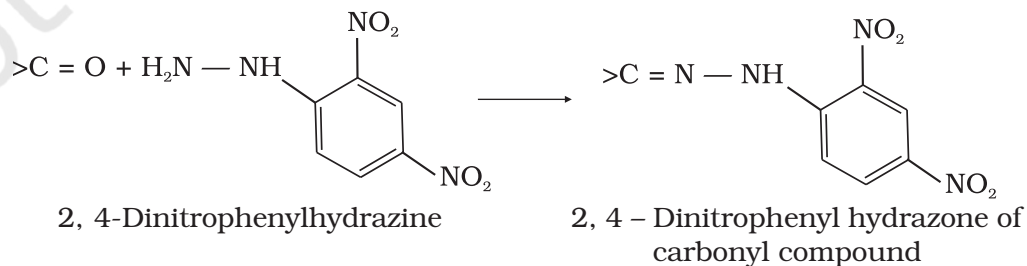
(R = alkyl, aryl or $\text{C}_6\text{H}_5\text{NH}$ etc.)

These reactions are catalysed by an acid or a base and do not occur under strongly acidic or basic conditions. Each reaction requires an optimum pH for its occurrence. Therefore, maintenance of pH is very important while carrying out these reactions.

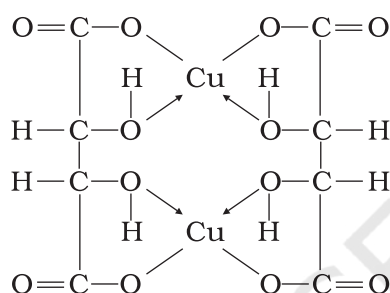
As far as oxidation is concerned, aldehydes are easily oxidised to carboxylic acids while ketones require relatively stronger oxidising agents. Distinction can be made between these two types of carbonyl compounds on the basis of difference in their reactivity.

Following tests are performed for the identification of aldehydic and ketonic groups:

- (i) On reaction with 2,4-dinitrophenylhydrazine (2,4-DNP), they form the respective 2,4-dinitrophenyl hydrazones.



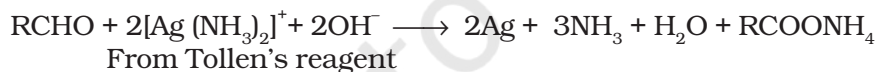
These two carbonyl compounds (aldehydes and ketones) are distinguished on the basis of tests using mild oxidising reagents, like Tollen's reagent and Fehling's reagent or Benedict's reagent. Tollen's reagent is an alkaline solution of silver cation complexed with ammonia, and Fehling's and Benedict's reagents are alkaline solutions containing cupric ions complexed with tartarate and citrate ions respectively. Fehling's reagent is freshly prepared by mixing equal amounts of Fehling's solution A and Fehling's solution B. Fehling's reagent deteriorates on keeping while Fehling's solutions A and B are quite stable. Fehling's solution A is an aqueous copper sulphate solution while Fehling's solution B is an alkaline solution of sodium potassium tartarate (Rochelle's salt). The reagent contains Cu^{2+} ion complexed with tartarate ions. The structure of the complex is given below :



Copper tartarate complex

Benedict modified the original Fehling's test by using a single solution which is more convenient for the test. Benedict's solution is more stable than Fehling's reagent and can be stored for a long time. It is an alkaline solution containing a mixture of copper sulphate and sodium citrate ($2\text{Na}_3\text{C}_6\text{H}_5\text{O}_7 \cdot 11\text{H}_2\text{O}$).

Complex formation decreases the cupric ion concentration below that necessary for precipitation of cupric hydroxide. These two reagents oxidize aldehydes while ketones remain unaffected. The chemistry of these tests is as follows:



However, aromatic aldehydes do not give positive Fehling's test. In Benedict test also, Cu^{2+} ions are reduced to Cu^+ ions in the same manner as in the case of Fehling's reagent.

Aldehydes also give pink colour with Schiff's reagent (the reagent is prepared by decolourising aqueous solution of *p*-rosaniline hydrochloride dye by adding sodium sulphite or by passing SO_2 gas). Ketones do not respond to this test.

Material Required

- Beaker (250 mL) : One
- Test tube holder : One
- Test tubes : As per need



- Schiff's reagent : As per need
- Fehling's solutions A and B: As per need
- Silver nitrate : As per need
- Dilute ammonium hydroxide solution : As per need
- 2,4-Dinitrophenylhydrazine reagent : As per need

Silver nitrate



Ammonia solution



Ammonia gas

**Procedure****A. Test given by both aldehydes and ketones***2,4-Dinitrophenylhydrazine test (2,4-DNP test)*

Take 2-3 drops of the liquid compound in a test tube or in case of solid compound, dissolve a few crystals of it in 2-3 mL alcohol. Add a few drops of an alcoholic solution of 2,4-dinitrophenylhydrazine. Appearance of yellow, orange or orange-red precipitate confirms the presence of carbonyl group. If precipitate does not appear at room temperature, warm the mixture in a water bath for a few minutes and cool.

B. Tests given by aldehydes only

Following tests namely Schiff's test, Fehling's test and Tollen's test are given by aldehydes only.

Schiff's test

Take 3-4 drops of the liquid compound or dissolve a few crystals of organic compound in alcohol and add 2-3 drops of the Schiff's reagent. Appearance of pink colour indicates the presence of an aldehyde.

Fehling's test

Take nearly 1 mL of Fehling's solution A and 1 mL of Fehling's solution B in a clean dry test tube. To this add 2-3 drops of the liquid compound or about 2 mL of the solution of the solid compound in water or alcohol. Heat the content of the test tube for about 2 minutes in a water bath. Formation of brick red precipitate of copper (I) oxide indicates the presence of an aldehyde. This test is not given by aromatic aldehydes.

Benedict's test

Add 5 drops of the liquid compound or the solution of the solid organic compound in water or alcohol to 2 mL Benedict's reagent. Place the test tube in boiling water bath for 5 minutes. An orange-red precipitate indicates the presence of an aldehyde.

Tollen's test

- (i) Take 1 mL of freshly prepared (~ 2 %) silver nitrate solution in a test tube. Add 1-2 drops of sodium hydroxide solution to it and shake, a dark brown precipitate of silver oxide appears. Dissolve the precipitate by adding ammonium hydroxide solution drop-wise.
- (ii) To the above solution, add an aqueous or an alcoholic solution of the organic compound.
- (iii) Heat the reaction mixture of step (ii) in a water bath for about 5 minutes. Formation of a layer of silver metal on the inner surface of the test tube which shines like a mirror, indicates the presence of an aldehyde.

Precautions

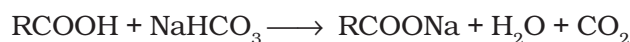
- (a) Always use freshly prepared reagents to perform the tests.
- (b) Do not heat the reaction mixture directly on a flame.
- (c) After performing the test, destroy the silver mirror by adding dilute nitric acid and drain off the solution with excess of water.

V. CARBOXYL GROUP (—COOH)**Theory**

Organic compounds containing carboxyl functional groups are called carboxylic acids.

The term carboxyl, derives its name from the combination of words carbonyl and hydroxyl because carboxylic functional group

contains both of these groups ($\text{—}\overset{\text{O}}{\parallel}\text{C—OH}$). These acids turn blue litmus red and react with sodium hydrogencarbonate solution to produce effervescence due to the formation of carbon dioxide. This is a test that distinguishes carboxylic acids from phenols.



VI. AMINO GROUP ($-\text{NH}_2$)

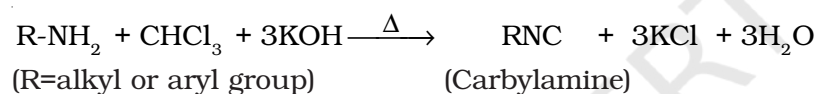
Theory

Organic compounds containing amino group are basic in nature. Thus they easily react with acids to form salts, which are soluble in water.

Both, aliphatic and aromatic amines are classified into three classes namely— primary ($-\text{NH}_2$), secondary ($-\text{NH}-$) and tertiary ($-\text{N}<$), depending upon the number of hydrogen atoms attached to the nitrogen atom. Primary amine has two hydrogen atoms, secondary has one while tertiary amine has no hydrogen atom attached to nitrogen.

(i) Carbylamine test

Aliphatic as well as aromatic primary amines give carbylamine test in which an amine is heated with chloroform.

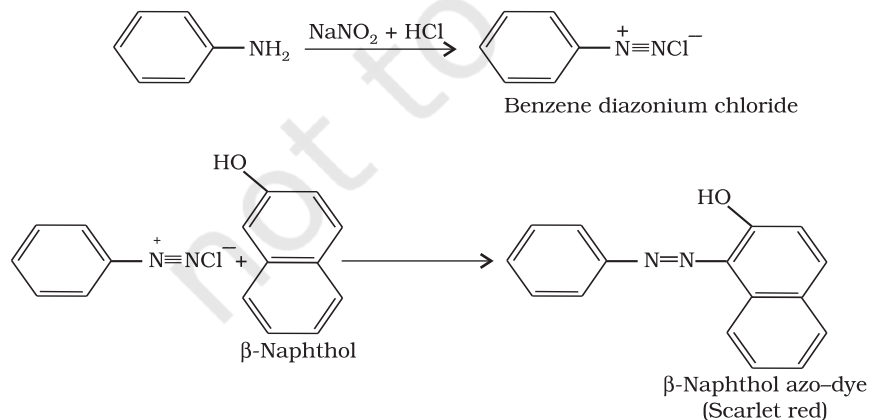


Caution!



Carbylamine so formed is highly toxic and should be destroyed immediately after the test. For this cool the test tube and add carefully an excess of conc. HCl.

(ii) Azo dye test

Aromatic primary amines can be confirmed by azo dye test. Primary amine e.g. aniline reacts with nitrous acid generated in situ by the reaction of sodium nitrite with HCl at $0-5^\circ\text{C}$ to produce diazonium salt. This couples with β -naphthol to give a scarlet red dye, which is sparingly soluble in water.



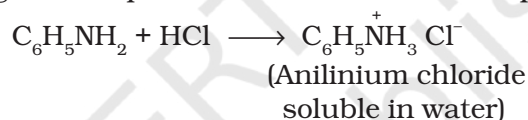
Material Required

	<ul style="list-style-type: none"> • Test tubes : As per need • Test tube holder : One • Bunsen burner : One 		<ul style="list-style-type: none"> • Chloroform • Potassium hydroxide • Sodium nitrite solution • Aniline • β-Naphthol • Dilute hydrochloric acid • Sodium hydroxide solution • Ice 	} As per need
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Procedure

A. Solubility test

Take 1 mL of given organic compound in a test tube and add a few drops of dilute HCl to it. Shake the contents of the test tube well. If the organic compound dissolves, it shows the presence of an amine.



B. Carbylamine test

Take 2-3 drops of the compound in a test tube and add 2-3 drops of chloroform followed by addition of an equal volume of 0.5 M alcoholic potassium hydroxide solution. Heat the contents gently. An obnoxious smell of carbylamine confirms the presence of primary amino group in the compound.

Caution!

Do not inhale the vapours. Destroy the product immediately by adding concentrated hydrochloric acid and flush it into the sink.

C. Azo dye test

- (i) Dissolve nearly 0.2 g of the compound in 2 mL of dilute hydrochloric acid in a test tube. Cool the content of the test tube in ice.
- (ii) To the ice cooled solution add 2 mL of 2.5% cold aqueous sodium nitrite solution.
- (iii) In another test tube, dissolve 0.2 g of β-naphthol in dilute sodium hydroxide solution.
- (iv) Add diazonium chloride solution prepared in step (ii) into the cold β-naphthol solution slowly with shaking.

The formation of a scarlet red dye confirms the presence of aromatic primary amine.

Chloroform 

Aniline 

Potassium hydroxide 

Sodium nitrite  

β-naphthol 

Precautions

- Do not expose yourself to the vapours while performing carbylamine test because isocyanide is highly poisonous. Destroy it immediately as described above.
- Maintain the temperature of the reaction mixture below 5°C during diazotisation, as diazonium chloride is unstable at higher temperatures.
- Always add diazonium chloride solution into the alkaline solution of β -naphthol and not vice-versa.

**Discussion Questions**

- What is Bayer's reagent?
- Why do alkenes and alkynes decolourize bromine water and alkaline KMnO_4 ?
- Explain why for the confirmation of unsaturation in a compound both the tests namely test with bromine water and test with Bayer's reagent should be performed.
- Why does phenol decolourize bromine water?
- How will you distinguish between phenol and benzoic acid?
- Why does benzene not decolourise bromine water although it is highly unsaturated?
- Why does formic acid give a positive test with Tollen's reagent?
- Outline the principle of testing glucose in a sample of urine in a pathological laboratory?
- Why is Benedict's reagent more stable than Fehling's reagent?
- How would you distinguish an aldehyde from a ketone by chemical tests?
- How would you separate a mixture of phenol and benzoic acid in the laboratory by using chemical method of separation?
- Write the chemistry of diazotisation and coupling reactions.
- How can you distinguish between hexylamine ($\text{C}_6\text{H}_{13}\text{NH}_2$) and aniline ($\text{C}_6\text{H}_5\text{NH}_2$)?
- How can you distinguish between ethylamine and diethylamine?
- How can CH_3OH and $\text{C}_2\text{H}_5\text{OH}$ be distinguished chemically?
- Why is solution of iodine prepared in potassium iodide and not in water?
- What is haloform reaction? What type of compounds generally give this reaction?
- How can you distinguish the compounds $\text{CH}_3-\overset{\text{O}}{\parallel}{\text{C}}-\text{C}_2\text{H}_5$ and $\text{C}_2\text{H}_5-\overset{\text{O}}{\parallel}{\text{C}}-\text{C}_2\text{H}_5$ by simple chemical test?