

EXPERIMENT - 15

To Identify the Functional Groups present in the given organic compounds and perform:

- (i) Test for unsaturation.
 - (ii) Test for carboxylic, phenolic, aldehydic and ketonic groups.
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15.1 OBJECTIVES

After performing this experiment, you should be able to :

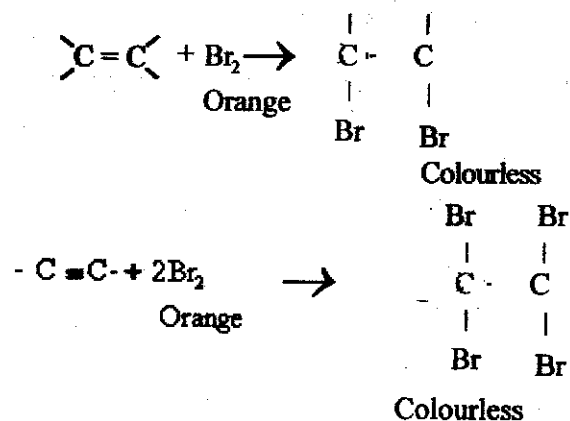
- *detect the presence of unsaturation in a given organic compound by simple tests ;*
- *differentiate between saturated and unsaturated compounds ;*
- *detect the presence of the following functional groups in the given organic compounds: carboxylic, phenolic, aldehydic and ketonic groups ;*
- *differentiate between the pairs of compounds containing (a) carboxylic and phenolic groups and (b) aldehydic and ketonic groups ;*
- *explain the acidic nature of carboxylic and phenolic groups ;*
- *write the reactions involved in the various tests.*

15.2 WHAT YOU SHOULD KNOW ?

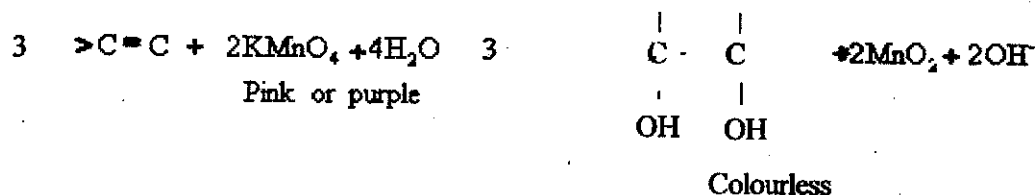
In an organic compound, unsaturation is due to the presence of double ($>C=C<$) or triple ($-C\equiv C-$) bonds in the molecule. The presence of unsaturation is tested by the following two methods.

- (i) Bromine water test
- (ii) Baeyer's test (using 1% alkaline potassium permanganate solution)

(i) **Bromine water test :** The organic compound is treated with bromine water dropwise. The decolourisation of bromine water shows the presence of unsaturation in the organic compound.



(ii) **Baeyer's test:** The organic compound is treated with an aqueous solution of alkaline potassium permanganate (Baeyer's reagent). The disappearance of the pink colour of potassium permanganate shows the presence of unsaturation.



Precautions

1. Do not inhale the bromine water or bromine in carbontetrachloride.
2. If the compound is soluble in water, use bromine water for testing. If the compound is insoluble in water, then dissolve 0.5 ml of the compound (liquid) or a pinch of the solid in 1 ml of carbon tetrachloride and test it with bromine in carbon tetrachloride solution.
3. Add the reagents dropwise.

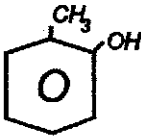
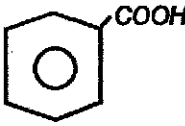
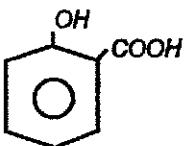
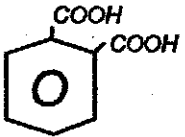
15.2.1 Functional Group

A functional group is that part of the compound which contains an atom or a group of atoms and shows specific reactions. It is the reactive part of a given compound where as the hydrocarbon part is the non-reactive part. For example, in $\text{CH}_3 - \text{CH}_2 - \text{CH}_2 - \text{COOH}$

$\text{CH}_3 - \text{CH}_2 - \text{CH}_2 -$ is the non-reactive hydro carbon chain, while- COOH is the functional group called carboxylic acid group.

All the reactions of $\text{CH}_3\text{CH}_2\text{CH}_2\text{COOH}$ are due to the presence of - COOH group.

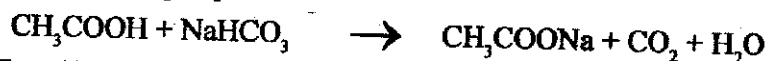
In the following section, we shall discuss the chemistry of four functional groups, phenolic(-OH) carboxylic (-COOH), aldehydic (-CHO) and ketonic $\text{C}=\text{O}$. The examples of compounds containing these groups are given in the following table.

Functional Group	Class of the Compound	Specific Examples
$\text{C} - \text{OH}$ Phenolic	Phenols	$\text{C}_6\text{H}_5 - \text{OH}$ Phenol  2-cresol
$\begin{array}{c} \text{O} \\ \\ \text{C} - \text{OH} \end{array}$ Ethanoic acid Carboxylic acid group	Carboxylic acids	CH_3COOH  Benzoic acid  Salicylic acid  Phthalic acid
$\begin{array}{c} \text{H} \\ \\ \text{C} = \text{O} \end{array}$ Aldehydic	Aldehydes	CH_3CHO Ethanal $\text{C}_6\text{H}_5\text{CHO}$ Benzaldehyde
$> \text{C} = \text{O}$ Ketonic	Ketones	CH_3COCH_3 Propanone $\text{C}_6\text{H}_5 - \text{COCH}_3$ Acetophenone

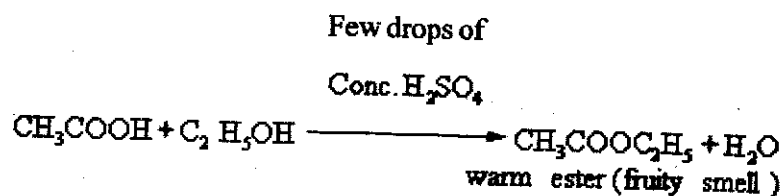
(A) Test for carboxylic group

The carboxylic group can be tested by the tests given on the next page :

- (i) **Litmus test** : Put a drop of an aqueous solution of the compound on blue litmus paper. If the blue litmus turns red, acidic nature is indicated.
- (ii) **Sodium hydrogen carbonate test** : Add a saturated solution of sodium hydrogen carbonate to an aqueous solution of the compound. If brisk effervescence appear due to evolution of CO_2 gas, the carboxylic group is confirmed.



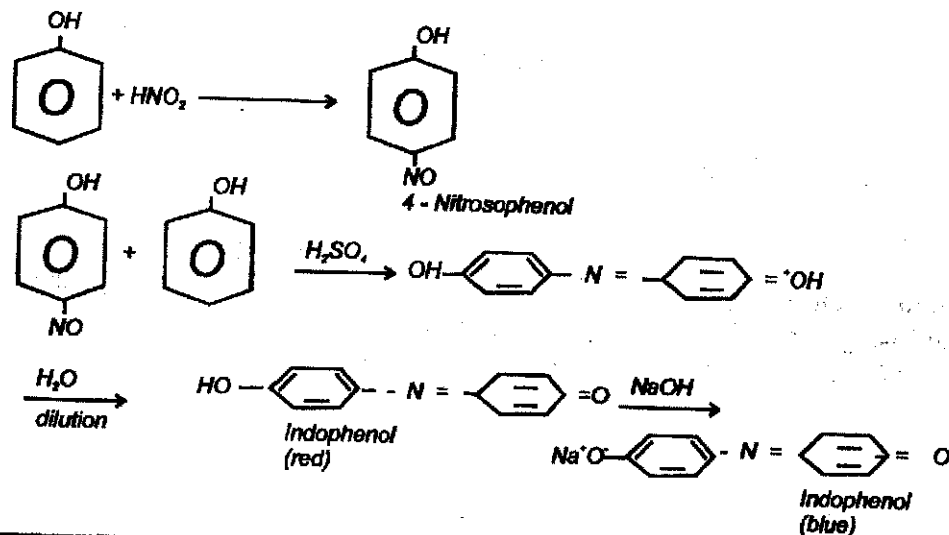
- (iii) **Esterification test** : The given organic compound is mixed with absolute ethanol in equal amounts and a few drops of conc. sulphuric acid are added. The mixture is warmed on a water bath. If a fruity smell (pleasant sweet smell) is obtained, the presence of carboxylic group is confirmed.

**(B) Tests for phenolic group**

- (i) **Ferric chloride test**: Dissolve a pinch of organic compound in water or alcohol. A few drops of this solution are mixed with neutral ferric chloride solution. If a red, blue or violet colouration appears, then the presence of phenolic group is confirmed.

For example, thus, red colouration is obtained with phenol while, with o-, m- and p-cresol, it is violet. With Resorcinol, gives blue colouration whereas catechol gives green colouration.

- (ii) **Liebermann's Test**: The organic compound is mixed with solid sodium nitrite (2-3 crystals) and gently warmed for a few seconds. The mixture is cooled and conc sulphuric acid is added. The solution appears red in colour on dilution with water and the colour changes to blue / green on treatment with sodium hydroxide. The above observation confirms the presence of phenolic group in the given compound.

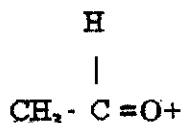


(C) Tests for aldehydes and ketones

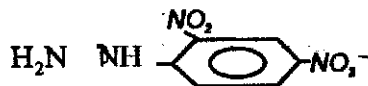
Both aldehydes and ketones contain the carbonyl group ($>C=O$). The carbonyl group can be confirmed by:

- (i) 2,4-dinitrophenylhydrazine (2,4-DNP test)
- (ii) Sodium bisulphite

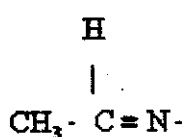
(i) **2,4-DNP test**: The organic compound is treated with 2,4-DNP reagent and warmed over a water bath. Formation of yellow or orange crystals indicate the presence of a carbonyl group (aldehydic or ketonic).



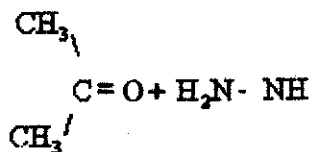
Ethanal



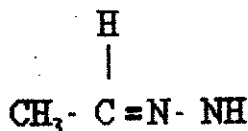
2,4-Dinitrophenylhydrazine



2,4-Dinitrophenylhydrazone of the aldehyde



Propanone 2,4Dinitrophenyl hydrazine

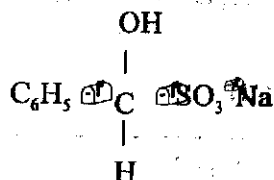


2,4-Dinitrophenyl hydrazone of the Ketone

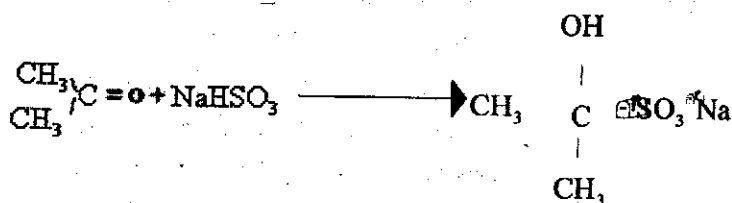
(ii) **Sodium bisulphite test**: The organic compound is treated with a saturated solution of sodium bisulphite. The mixture is shaken well and left for 15 minutes. The formation of a crystalline precipitate indicates the presence of a carbonyl group.

$C_6H_5CHO + NaHSO_3 \rightarrow$ indicates the presence of a carbonyl group.

Benzaldehyde



Addition product



Addition product

(A) Tests for Aldehydes

(i) **Fehling's test**: The organic compound is treated with Fehling's solution and warmed over a water bath. Appearance of a red / orange precipitate confirms the presence of aldehydic group.

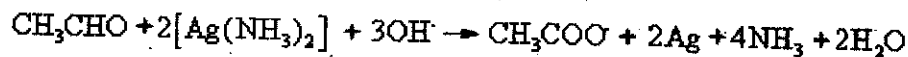


Acetaldehyde
Solution

Red precipitate

The aldehyde reduces the Cu^{2+} (cupric ions) to cuprous state in Cu_2O (cuprous oxide).

3. **Tollen's Reagent test**: To the organic compound, an equal amount of Tollen's reagent is added and the mixture is warmed on a water bath. Appearance of shining silver mirror on the inner walls of the test tube confirms the presence of aldehydic group.



Tollen's Reagent

Silver mirror

The Tollen's reagent (ammonical silver nitrate solution) contains silver ions. These are reduced by aldehydes to metallic silver.

(B) Test for ketone

Ketones do not give Fehling's and Tollen's tests. Ketones give the following two tests which are not given by aldehydes:

1. ***m*-Dinitrobenzene test**: To a mixture of finely powdered *m*-dinitrobenzene and an equal amount of organic compound, add dilute sodium hydroxide solution. The appearance of red colour indicates the ketonic group.

2. **Sodium nitroprusside test:** To the given organic compound, add sodium nitroprusside solution and a little sodium hydroxide solution. Appearance of red- violet colour confirms the presence of ketonic group.

15.3 MATERIALS REQUIRED

(1) Apparatus	(2) Chemicals
Test tubes, Test tube stand, Test tube holder, Water bath, Tripod stand.	Samples of organic compounds, Bromine water, Alkaline potassium permanganate solution, Neutral ferric chloride solution, Sodium nitrite (solid), Litmus paper, Sodium hydrogen carbonate, Alcohol, Conc. sulphuric acid, 2, 4-Dinitrophenylhydrazine solution, sodium bisulphite solution, <i>m</i> -Dinitrobenzene solid, Sodium nitroprusside, Sodium hydroxide (10% solution), Fehling's reagent, Schiff's reagent and Tollen's reagent.

15.4 HOW TO PERFORM THE EXPERIMENT

The tests should be performed systematically as described in the following table. All functional groups should be tested. The experiments performed should be recorded as shown below:

Table 1: Tests for Unsaturation

Experiment	Observations	Inference
(a) To a solution of 0.2 g of the organic compound in water or CCl_4 , add bromine water or bromine in CCl_4 dropwise. Shake the mixture after each addition.	Bromine is decolourised	Unsaturation present
	or Bromine is not decolourised	or Unsaturation absent
(b) To the organic compound (0.5 g), add 1 ml of 0.5% aq. KMnO_4 solution dropwise	KMnO_4 solution is decolourised	Unsaturation present
	or KMnO_4 solution is not decolourised	or Unsaturation absent

Table 2: Test for phenolic hydroxyl group

Experiment	Observations	Inference
(a) Dissolve 50 mg of organic compound in 1-2 ml of water or alcohol. Put a drop of the solution on blue litmus paper.	Blue litmus turns red or No change	Compound is acidic in nature; May be phenolic OH group or carboxylic acid or phenolic OH or carboxylic group absent
(b) To a solution of the compound in water or alcohol add a drop of freshly prepared neutral ferric chloride solution	blue, green, violet or pink colouration appears or (no characteristic colouration)	Phenolic OH group present or Phenolic OH group absent
(c) (i) Heat about 50 mg of the organic compound with sodium nitrite (2-3 crystals) gently for 30 seconds in a dry test tube. To the cooled mixture, add 1 ml conc. H_2SO_4 .	Deep blue or green colouration appears	Phenolic group present
(ii) Add about 2-3 ml water to the above mixture	The colour changes to red	Phenolic OH group present
(iii) Add NaOH solution to the above mixture	Blue or green colour or negative test	Phenolic OH group absent if the test is negative

Precautions:

1. Phenol is highly corrosive. It causes blisters on the skin Always handle it carefully.
2. Neutral ferric chloride should be freshly prepared, see Appendix for details.
3. Phenol turns blue litmus red. Carboxylic acids also give the test but phenol does not decompose sodium hydrogen carbonate.
4. Instead of phenol, naphthols may be given for test for phenolic group.

Table 3: Test for carboxylic acids

Experiment	Observations	Inference
(a) The aqueous solution of the organic compound is put on a blue litmus paper	Blue litmus turns red or No change	- COOH group may be present - COOH group absent
(b) To the 0.2 g organic compound, add saturated solution of sodium bicarbonate	Effervescences seen or No effervescences	- COOH group present or - COOH group absent
(c) <i>Ester formation</i> To 0.2 g of the organic compound,	Fruity odour develops or	- COOH group present

add an equal amount of ethyl alcohol and a drop of conc. sulphuric acid. Warm the mixture on a water bath.

No fruity odour

- COOH group absent

Table 4: Tests for aldehydes and ketones

(a) To the solution of the organic compound (1 ml) add 5 ml 2, 4-dinitrophenylhydrazine reagent. Heat the solution in a water bath.	Yellow or orange precipitate	carbonyl group present (- CHO or > CO) > C = O
(b) The organic compound (0.5 g) is shaken with 2 ml of saturated sodium bisulphite solution.	white precipitate	- CHO, > C = O present
(c) To a solution of equal volumes of Fehling's A and Fehling's B, add 0.2 g of the organic compound. Heat the mixture for 5 minutes in a water bath.	Red precipitate of Cu_2O	Aldehyde (- CHO) group present
(d) To 1 ml of AgNO_3 solution, add a drop of dil. NaOH solution. To this, add ammonium hydroxide dropwise till the precipitate dissolves. To the resulting solution add 0.1 g of the organic compound. Heat for 5 minutes in a water bath.	Silver mirror is formed on the inner side of the test tube.	Aldehyde (- CHO) group present
(e) Add 1 ml of sodium nitroprusside solution to 0.5 g of the organic compound. Shake the mixture and add NaOH solution dropwise	red colour	Ketone (> C = O) group present
(f) Mix 0.1g of the organic compound with 0.1 g m-dinitrobenzene. Add 1 ml dil. NaOH soln. and shake	Violet colour fades slowly	Ketone (> C = O) group present

Precautions

1. Tollen's reagent should be freshly prepared.
2. Benzaldehyde reacts very slowly and a grey precipitate is generally obtained. Shake the tube vigorously to break the oily globules from time to time.
3. Wash the test tube thoroughly with warm sodium hydroxide solution followed by washing it with a large amount of water.

Specific Examples**(This is not a part of the experiment.)****Example 1:**

Aim of the Experiment : To identify by chemical tests which one of the samples, A and B is benzaldehyde and which one is acetone.

Apparatus : Test-tubes

Chemicals : Silver nitrate solution, Ammonium hydroxide, Iodine solution and Sodium hydroxide.

Observations : Perform the following chemical tests with compounds A and B.

Experiment	Observation	
	Compound A	Compound B
1. Colour and physical state	Colourless liquid (turns yellow on standing)	Colourless liquid
2. Odour	Odour of bitter almonds	Pleasant smell
3. Solubility in		
(i) Water	Immiscible	Miscible
(ii) Sodium hydroxide solution	Immiscible	Immiscible
(iii) 5% NaHCO ₃ solution	Immiscible	Immiscible
(iv) Conc. HCl	Immiscible	Immiscible
4. Chemical Test		
(i) Tollen's Test : (a) Place 1 ml of silver nitrate solution in a clean test-tube and add 1 drop of dil. NaOH solution. A brown ppt. is formed. Add ammonia solution dropwise until the brown ppt. just redissolves. To this add about 0.5 ml of liquid A and warm the test-tube in a beaker of boiling water for 5 minutes.	A shining silver mirror forms	
(b) Repeat this test with liquid B		No silver mirror
(ii) Sodium nitroprusside test: Add 1 ml of sodium nitroprusside to 0.5 ml of the liquid A and B in separate test tubes. Add NaOH	No characteristic colour	Red colour formation

solution to both the test tubes and shake them.

- (iii) (a) Mix 0.5 ml of the liquid B with 0.5 g of solid *m*-dinitrobenzene. Add NaOH and shake the contents. Violet colouration appears that fades slowly
- (b) Repeat the same with liquid A. No characteristic colour

Conclusion : Compound A is benzaldehyde and Compound B is Acetone.

Example 2 :

Aim of the Experiment : To identify by chemical tests which one of the samples C and D is phenol and which one is benzoic acid.

Apparatus : Test tubes

Chemicals. Sodium nitrite, Sodium bicarbonate

Observations

Experiment	Observations	
	Compound C	Compound D
1. Colour and physical state	Colourless or pink crystalline solid	White solid
2. Odour	Carbolic	Odourless
3. Solubility in:		
(i) Water	Sparingly soluble, forms an emulsion	Sparingly soluble
(ii) Dil. NaOH solution	Insoluble	Soluble
(iii) 5% NaHCO ₃ solution	Insoluble	Soluble
(iv) Conc. HCl	Insoluble	Soluble
4. Blue litmus test	Turns red	Turns red
5. Chemical tests		
(i) <u>Liebermann's test.</u>		
(a) Perform Liebermann's test with a portion of compound C. For procedure, see experiment in table	Deep blue or green colour	

(b) Repeat this test with a portion of compound D

No colouration

(ii) **Sodium bicarbonate test**

(a) Place 3 ml of 10% NaHCO_3 soln. in a clean test-tube and add a portion of the compound C. Warm it.

No effervescences

(b) Repeat this test with a portion of compound D.

Strong effervescences

Conclusion

The given organic compound was found to contain functional group.

15.5 CHECK YOUR UNDERSTANDING

1. Name the functional group (s) present in the following compounds.
Phenol, benzoic acid, salicylic acid and acetone

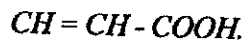
2. How will you distinguish the following pairs of compounds?

(a) Acetone and acetaldehyde.

(b) Acetic acid and phenol.

3. Write the reaction for bromine water test on $\text{C}_6\text{H}_5 - \text{CH} = \text{CH}_2$

4. What tests would be given by the following compound?



5. What is Baeyer's reagent?

6. Why should Tollen's reagent be freshly prepared?

7. Which compound is more acidic. Phenol or benzoic acid ?

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8. How will you differentiate between phenol and cresols ?

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9. How will you infer the presence of carbonyl group in a compound ?

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10. Give an example of aromatic is a methyl ketone.

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15.6 NOTE FOR THE TEACHER

1. The students may be given enough number of samples of the same functional group for proper practice.
2. Phenol is highly corrosive. For the test for phenolic groups, the students may be given - Naphthol, - Naphthol, or o -, m -, p - cresols etc. Avoid giving phenol directly to the students without proper precautions of handling.
3. Students should be told to wear lab coats and use gloves when corrosive substances are being handled.
4. The students and the assistant should be instructed to keep inflammable liquids away from the burner.
5. A sample worksheet is given in this section. The students may be asked to record the experiments in this format.

15.7 CHECK YOUR ANSWERS

Ans.1. The functional groups present in the following compounds are :

Phenol - Phenolic group.

Benzoic acid - Carboxylic acid group

Salicylic acid - Phenolic group and carboxylic group.

Acetone - Ketonic group.

Ans.2. Acetone and Acetaldehyde can be distinguished by any of the following tests.

(i) Fehling's test

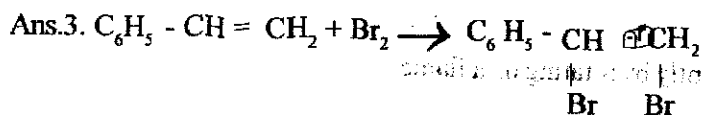
(ii) Tollen's test

(iii) Sodium nitropruside test

(iv) *m*-dinitro benzene test

The changes observed are tabulated below :

S. No.	Test performed	Acetaldehyde	Acetone
a.	Fehling's test	red colouration appears	×
b.	Tollen's test	Silver mirror is formed	×
c.	Sodium nitropruside test	×	Violet colouration
d.	2,4-dinitrobenzene test	×	red colouration



Ans.4. $CH = CH - COOH$ will give the following tests:



(i) Positive test for unsaturation due to the double bond.

(ii) Positive test for carboxylic group.

The compound will therefore, give positive test with bromine water and positive test with sodium hydrogen carbonate.

Ans.5. Baeyer's reagent is an alkaline solution of potassium permanganate. (please see appendix for details)

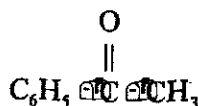
Ans.6. Tollen's reagent is a solution of ammoniacal silver nitrate. It should be freshly prepared because it is unstable as it can easily decompose to Ag_2O and finally to silver, on standing.

Ans.7. Benzoic acid is a stronger acid than phenol. Benzoic acid will give brisk effervescences with sodium hydrogen carbonate solution due to the liberation of carbon dioxide gas. Phenol does not give positive test with sodium hydrogen carbonate as it is a weak acid.

Ans.8. Phenol and cresols can be differentiated by neutral ferric chloride test. Phenol will give red colouration, o-, m- and p-cresol will give violet colouration.

Ans.9. Carbonyl compounds give 2, 4-dinitrophenylhydrazine test and sodium bisulphite test. Crystalline precipitates are formed in both cases.

Ans.10. Acetophenone is an example of methyl ketone. It has the formula



4. CHECK YOUR ANSWERS

Ans. 1 Multiple scratches, if made on the glass tube will cause a rough and irregular cut.

Ans. 2 The outer diameter of the borer should be equal to the inner diameter of the tube to be inserted into the bore.

Ans. 3 To avoid cracking of the cork and to get a smoother bore, it is moistened with water and pressed in a cork presser.

Ans. 4 The edges should be heated gently by rotating on a flame.
