

# Identification of a Pure Organic Compound

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Chapter 3



# **Basic Concepts**

Organic compounds can be classified in respect of their physical state, solubility, physical and chemical properties. A particular compound responds to a specified reaction, but the same reaction may not be applicable to other compounds. Difference in solubility coupled with response to a specific reaction involving visible change may be an effective tool for the identification of pure organic compound. The present chapter deals with identification of pure organic compounds utilising the aforesaid criteria.



# Tests for Known Solid Organic Compound

# 3.2.1 Oxalic acid

Physical Characteristics		
1. State Crystalline solid		
2. Colour	White	
3. Odour	Odourless	
4. Solubility	Soluble in cold water	

#### Chemical Tests:

Experiment	Observation
1. A pinch of the sample is added to a saturated solution of sodium bicarbonate.	Effervescence
2. A few drops of conc. H <sub>2</sub> SO <sub>4</sub> is added to an aqueous solution of the sample. Then a few drops of dilute potassium permanganate solution is added to it.	Decolourisation of the pink colour of permanganate.
3. An aqueous solution of the sample is made ammoniacal and then an aqueous solution of calcium chloride is added to it.	White crystalline precipitate

	Observation
4. Denige's reagent is added to an aqueous solution of the sample.	Immediate formation of white precipitate.
5. A pinch of the sample is heated with a few drops of conc. sulphuric	The gas burns with blue
acid and the issuing gas is ignited.	name.

### Reactions:

1. Reaction with sodium bicarbonate:

$$\begin{array}{cccc}
\text{COOH} & + \text{NaHCO}_3 & \longrightarrow & \text{COONa} \\
\text{COOH} & + \text{COONa} & + \text{CO}_2 + \text{H}_2\text{O} \\
\text{COONa} & & \text{COONa}
\end{array}$$

2. Reaction with potassium permanganate:

COOH + 
$$KMnO_4 + H_2SO_4 \longrightarrow CO_2 + K_2SO_4 + MnSO_4 + H_2O$$

3. Reaction with calcium chloride:

COOH
$$| + NH_4OH + CaCl_2 \longrightarrow (COO)_2Ca + NH_4Cl + H_2O$$
COOH
White ppt

4. Denige's test:

5. Reaction with concentrated sulphuric acid:

COOH  

$$| + H_2SO_4 \rightarrow CO + CO_2 + H_2O + H_2SO_4$$
  
COOH  
Burns with  
blue flame



Physical C	haracteristics
1. State	Crystalline solid
2. Colour	White
3. Odour	Odourless
4. Solubility	Soluble in cold water

# Chemical Tests:

Experiment	Observation
1. A pinch of the sample is added to a saturated solution of sodium bicarbonate.	A STATE OF THE STA
2. One part of the sample is mixed with two parts of resorcinol. The mixture is heated to melt. Then a few drops of conc. H <sub>2</sub> SO <sub>4</sub> is added to the melt and heated again. The mixture becomes dark red. It is then added to a large excess of dilute NaOH. (Fluorescence test)	Intense fluorescence wi greenish tint.

Experiment	Observation
3. An aqueous solution of the sample is made ammoniacal and then an aqueous solution of calcium chloride is added to it. The mixture is boiled and inner wall of the test tube is scratched with a glass rod	tate after boiling and cool-
4. 4. Denige's reagent is added to an aqueous solution of the sample,	No precipitate,
The solution is then boiled, cooled and treated with a few drops of dilute aqueous solution of potassium permanganate.	Pink colour of permanga- nate persists.

#### Reaction:

# 1. Reaction with sodium bicarbonate:

$$\begin{array}{c} \text{COOH} \\ \text{COOH} \end{array}$$
 + NaHCO<sub>3</sub>  $\longrightarrow$   $\begin{array}{c} \text{COONa} \\ \text{COONa} \end{array}$  + CO<sub>2</sub> + H<sub>2</sub>O

#### 2. Fluorescence test:

## 3. Reaction with calcium chloride:

White precipitate

Green fluorescence

# 32.5 Resorcinol

Physical Characteristics		
1. State	Solid flake shaped	
2. Colour	Light brown	
3. Odour	Odourless	
4. Solubility	Soluble in cold water	

#### **■** Chemical Tests:

Experiment	Observation
1. A few drops of freshly prepared solution of ferric chloride is added to an aqueous solution of the sample.	Violet colouration
and shaken well	Aqueous layer turns wine red. On acidification with conc. HCl the red colour disappears with the formation of light yellow colour.
	Intense fluorescence with greenish tint.

#### ■ Reaction:

#### 1. Reaction with ferric chloride:

HO OH FeCl<sub>3</sub> 
$$\begin{bmatrix} OH \\ Violet \end{bmatrix}$$
 Fe

#### 2. Reaction with chloroform:

# 3. Fluorescence test:

Physical Characteristics		
1. State	Crystalline solid	
2. Colour	White	
3. Odour	Characteristics odour	
4. Solubility	Soluble in cold water	

#### **■** Chemical Tests:

Experiment	Observation
1. The sample is heated strongly.	Smell of ammonia perceived.
2. The sample is heated to a melt. The melt is allowed to solidify. It is dissolved in water. One or two drops of NaOH solution is added to it followed by addition of a few drops of a very dilute aqueous solution of copper sulphate. (Biuret Test)	Violet colouration
<b>3.</b> The sample is dissolved in dilute HCl. Then a saturated aqueous solution of sodium nitrite is added to it.	Evolution of colourless, odourless gas.
<ol><li>Concentrated nitric acid is added to an aqueous solution of the sample.</li></ol>	White precipitate

#### Reaction:

#### 1. Action of heat:

$$H_2NCONH_2 \xrightarrow{\Delta} CO_2 + NH_3 + H_2O$$

### 2. Biuret Reaction:

Violet

#### 3. Reaction with sodium nitrite:

$$H_2NCONH_2 + NaNO_2 + HCl \rightarrow CO_2 + H_2O + N_2 + NaCl$$

# 4. Reaction with concentrated nitric acid:

White preciptiate



Physical Characteristics		
1. State Amorphous solid		
2. Colour	White	
3. Odour	Odourless	
4. Solubility	Soluble in cold water	

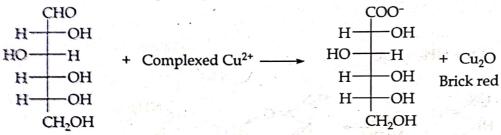
#### ■ Chemical Tests:

Experiment	Observation
1. The sample is added to a mixture of Fehling A and Fehling B and heated for 1 minute.	Brick red precipitate.
2. The sample is heated with Benedict's reagent for 1 minute.	Brick red precipitate.

Experiment	Observation
3. The sample is heated with Barfoed's reagent for 1 minute.	Brick red precipitate
4. The sample is dissolved in an ethanolic solution of $\alpha$ -naphthol or $\beta$ -naphthol. Then conc. H <sub>2</sub> SO <sub>4</sub> is added cautiously along the inner wall of the test tube (Molisch Test).	Violet to deep red colouration at the junction of two liquids.
5. The sample is added to Tollen's reagent and heated on a water bath.	Black or grey precipitate or shining silver mirror.
6. An aqueous solution of the sample is mixed with equal volume of glacial acetic acid. Phenyl hydrazine is added to it and warmed on a water bath for 2-3 minutes. Then the solution is cooled. (Osazone test).	Yellow precipitate.

#### Reaction:

### 1. Reaction with Fehling's reagent :



#### 2. Reaction with Benedict's reagent:

## 3. Reaction with Barfoed's reagent :

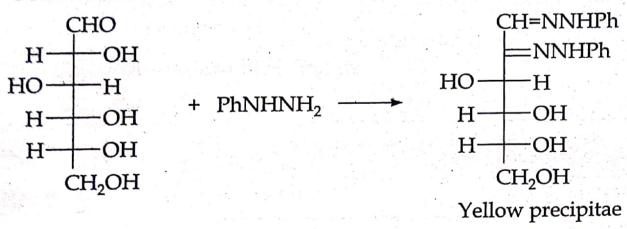
#### 4. Molisch test:

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# 5. Tollen's test:

CHO
H—OH
HO—H + 
$$[Ag(NH_3)_2]^+$$
NaOH
H—OH
CH<sub>2</sub>OH

## 6. Osazone test:



# 3.2.10 Salicylic acid

	Physical Characteristics
1. State	Crystalline solid
2. Colour	White
3. Odour	Odourless
4. Solubility	Insoluble in cold water, but soluble in hot water

4. Reaction with Tollen's Reagant:

Ago > 2Nano, + Ho + 4NH

ZAKNOS + ZVIJOH = ABCOT + ZVINOS + 11,0

# **■** Chemical Tests:

Experiment	Observation
1. A pinch of the sample is added to a saturated solution of sodium bicarbonate.	Effervescence
2. A few drops of freshly prepared solution of ferric chloride is added to an ethanolic solution of the sample.	Violet colouration
3. The sample is heated with methanol and 2-3 drops concentrated sulphuric acid and the solution is poured in large excess of water. (oil of wintergreen test)	Smell of oil of wintergreen is perceived

## 1. Reaction with sodium bicarbonate:

$$\begin{array}{c|c}
COOH \\
OH
\end{array}$$

$$\begin{array}{c|c}
COOH \\
+ CO_2 + H_2O
\end{array}$$

### 2. Reaction with ferric chloride:

# 3. Oil of wintergreen test:

Oil of wintergreen

# 3.3.2 Acetic acid

P	Physical Characteristics
1. State	Liquid
2. Colour	Colourless
3. Odour	Vinegar like smell
4. Miscibility	Completely miscible with water

# **■** Chemical Tests:

Experiment	Observation
1. To a little saturated aqueous sodium bicarbonate solution, few drops of given sample is added.	Effervescence
2. $\sim 1$ mL of given sample is mixed with $\sim 1$ mL of ethanol and few drops of conc. H <sub>2</sub> SO <sub>4</sub> . The mixture is heated carefully, and then poured into large excess of water taken in a beaker.	Fruity smell obtained.
3. Few drops of given sample is treated with sodium bicarbonate till effervescence is ceased and the solution is evaporated to dryness. The solid residue thus obtained is then heated with finely powdered arsenious oxide (Cacodyl oxide test).	A vapour with a very offen sive smell is given out.*

<sup>\*</sup> The vapour of cacodyl oxide is very much poisonous, so never inhale the smell directly; Put the thumb on the mouth of the test tube, then smell the thumb. As soon as the experiment is over, the thumb and the test tube should be washed thoroughly with large excess of water.

# Identification of a Pure Organic Compound

# Reactions:

1. Action with NaHCO<sub>3</sub>:

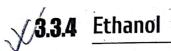
$$CH_3COOH + NaHCO_3 = CH_3COONa + CO_2 \uparrow + H_2O$$

2. Esterification test:

$$CH_3COOH + C_2H_5OH + [H_2SO_4] = CH_3COOC_2H_5 + H_2O + [H_2SO_4]$$

3. Cacodyl oxide test:

$$4CH_3COONa + As_2O_3 = H_3C As - O - As < CH_3 + 2CO_2 + 2Na_2CO_3$$



Physical Characteristics		
1. State	Liquid	
2. Colour	Colourless and the trains becomes and the second	
3. Odour	Pungent and faint alcoholic	
4. Miscibility	Completely miscible with water	

# **■** Chemical Tests:

Experiment	Observation
<ol> <li>A copper spiral is heated till red hot and plunged into ~ 2 mL of aqueous solution of given sample in a test tube placed in a beaker containing cold water. The whole process is repeated 3 - 4 times and the residual solution is cooled. The solution is then divided into two parts.</li> <li>(a) One part is treated with few drops of Schiff's reagent and shaken.</li> <li>(b) One part is treated with few drops of Tollen's reagent and slightly warmed.</li> </ol>	(a) Magenta colour develops which deepens on standing. (b) Black precipitate.
2. 2.~1 mL of given sample is mixed with ~1 mL of acetic acid and few drops of conc. H <sub>2</sub> SO <sub>4</sub> . The mixture is heated carefully, and then poured into large excess of water taken in a beaker.	Fruity smell obtained.
<ol> <li>~0.5 mL of concentrated iodine in KI solution is mixed with ~1 mL of given sample. To it, dil. NaOH solution is added drop by drop until the colour of iodine disappears.</li> </ol>	Light yellow precipitate with characteristic smell.

## ■ Reactions:

# 1. Copper coil oxidation and reaction with Schiff's reagent:

$$2Cu + O_2 = 2CuO$$

$$CH_3CH_2OH + CuO = CH_3CHO + H_2O + Cu$$

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$$HO_{2}SHN \xrightarrow{\text{NHSO}_{2}H} H_{3}C(HO)HCO_{2}SHN \xrightarrow{\text{NHSO}_{2}CH(OH)CH}_{3}$$

$$NHSO_{2}CH(OH)CH_{3}$$

$$NHSO_{2}H$$

Schiff's reagent (colourless)

Magenta colour

#### 2. Esterification test:

$$CH_3COOH + C_2H_5OH + [H_2SO_4] = CH_3COOC_2H_5 + H_2O + [H_2SO_4]$$

# 3. Reaction with iodine and NaOH (Iodoform test):

$$CH_3CH_2OH + 4I_2 + 6NaOH = CHI_3 \downarrow + HCOONa + 5NaI + 5H_2O$$
  
Light yellow

# 3.3.5 Acetone

Physical Characteristics		
1. State	Liquid	
2. Colour	Colourless	
3. Odour	Pungent and faint alcoholic	
4. Miscibility	Completely miscible with water	

#### **■** Chemical Tests:

Experiment	<b>Observation</b>
1. Few drops of 2,4-DNP solution is added to ~1 mL of given sample. A few drops of water is added to the reaction mixture.	Yellow precipitate.
2. ~0.5 mL of iodine in KI solution is mixed with ~1 mL of given sample. To it, 2-3 beads of solid NaOH is added and shaken well.	
3. ~1 mL of dil. NaOH solution is added to ~0.5 mL of aqueous solution of given sample and to it, 2-3 drops of sodium nitroprusside solution is added (Legal's test).	Ruby red colouration.

#### Reactions:

# 1. Reaction with 2,4-dinitrophenyl hydrazine (Brady's reagent):

$$H_3C$$
 $O + NO_2$ 
 $NO_2$ 
 $NO_2$ 
 $NO_2$ 
 $NO_2$ 
 $NO_2$ 
 $NO_2$ 
 $NO_2$ 
 $NO_2$ 
 $Yellow$ 

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# 2. Reaction with iodine and NaOH (Iodoform test):

 $CH_3COCH_3 + 3I_2 + 4NaOH = CHI_3 \downarrow + CH_3COONa + 3NaI + 3H_2O$ 

Light yellow

## 3. Reaction with sodium nitroprusside (Legal's test):

 $CH_3COCH_3 + Na_2[Fe\ (CN)_5NO] + OH^- = Na_2[Fe\ (CN)_5NOCH_2COCH_3] + H_2O$ 

Ruby red

# 3.3.6 Aniline

Physical Characteristics	
1. State	Liquid
2. Colour	Colourless when freshly distilled, gradually turns brown on exposure to light and air.
3. Odour	Characteristic smell
4. Miscibility	Immiscible with water*, miscible in dil. HCl

#### ■ Chemical Tests:

Experiment	Observation
1. To ~1 mL of given sample, few drops of bromine water is added.	
2. Few drops of given sample is dissolved in ~1 mL dil. HCl, cooled to 0-5°C followed by treatment with few drops of aqueous NaNO <sub>2</sub> solution. The resultant solution is then poured into alkaline $\beta$ -naphthol solution under cold condition. (Diazo-coupling test)	

### ■ Reactions:

# 1. Reaction with bromine:

$$NH_2$$
 $+3Br_2$ 
 $Br$ 
 $Br$ 
 $Br$ 
 $Br$ 
 $White$ 

# 2. Reaction with $\beta$ -naphthol (Diazo coupling test):

$$\begin{array}{c|c} & N = N - \\ \hline & N = N - \\ \hline & 0.5^{\circ}C \end{array}$$

$$\begin{array}{c|c} & N = N - \\ \hline & OH \end{array}$$

$$\begin{array}{c|c} & N = N - \\ \hline & OH \end{array}$$

$$\begin{array}{c|c} & Red \ dye \end{array}$$

<sup>\*</sup> Aniline has higher density than water, so it appears at the lower layer when shaken with water.

# 3.3.9 Nitrobenzene

	Physical Characteristics
1. State	Liquid
2. Colour	Pale yellow
3. Odour	Characteristic smell of bitter almond
4. Miscibility	Immiscible with water

# ■ Chemical Tests:

Experiment	Observation
1. Few drops of given sample is strongly boiled with a few granules of metallic tin and ~2 mL of conc. HCl. The mixture is cooled, diluted	Orange-red dye obtained.
with water and cooled to 0-5°C followed by treatment with few drops	
of saturated aqueous NaNO <sub>2</sub> solution. The resultant solution is then poured into alkaline $\beta$ -naphthol solution under cold condition.	

Experiment	Observation
2. An aqueous ethanolic solution of a few drops of given sample is	Grey or black precipitate
boiled with a pinch of zinc dust and little solid NH4Cl. The mixture	
is cooled and filtered into Tollen's reagent (Mulliken - Barker test).	

#### ■ Reactions:

1. Reduction in acid medium followed by diazo coupling test:

$$NO_2 = NH_2 \cdot HCI$$

$$N_2CI$$

$$N_3CI$$

$$N_4$$

$$N_2CI$$

$$N_2CI$$

$$N_4$$

2. Mulliken - Barker test: