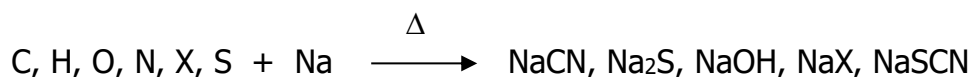


**Exp. 1****Elemental Analysis**

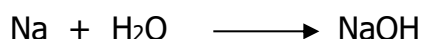
Elemental analysis is considered as an important step in the identification of organic compounds. The chief element in the organic compounds is carbon, hydrogen and oxygen for which we do not employ chemical tests. Next to them in order of importance are nitrogen, halogens (chlorine, bromine, fluorine and iodine), and sulfur that can be detected by reaction with sodium metal. The method is known as sodium fusion method.

The nonpolar nature of organic compounds makes the detection of N, S, and X difficult because organic compounds do not ionize in solution to give ions of these elements. For this reason it is necessary to convert these elements into inorganic ions before doing the tests. The conversion is accomplished by heating a small quantity of the organic compound with an equal quantity of metallic sodium. The organic compound will decompose and soluble sodium salts of the elements will be formed.



Sodium thiocyanide, NaSCN is produced when both sulfur and nitrogen are present in the same organic compound only when the quantity of sodium element is small.

Sodium element is very reactive and react with water vigorously resulting in explosion. So extreme care should be taken during the handling the metal.



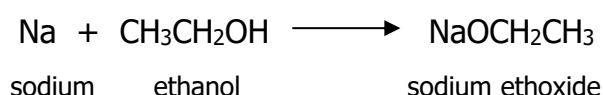
Therefore sodium element is kept dipped in liquid paraffin to prevent exposure to moisture. The paraffin should be wiped off before using the sodium. It is also advised not to touch it directly by hands since hands are usually moist, resulting in burning

sensation. Not that sodium is a shiny element and when it is exposed to air and moisture it is oxidized and become non shiny.

## Procedure

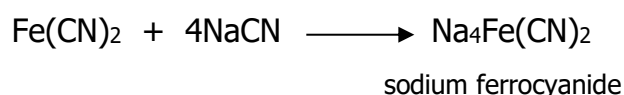
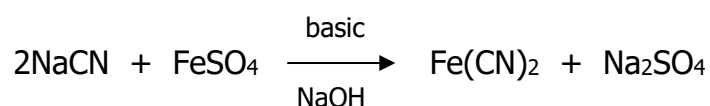
A small quantity of the unknown is placed in a clean dry test tube together with a small piece of sodium metal. The test tube is held vertically by a clamp. The lower part of the test tube is heated gradually until the sodium melts and its vapors fill the lower part of the tube. This gradual heating is to prevent the loss of the products as vapors. Heating is then continued for additional five minutes until the bottom of the test tube becomes red. Cautiously drop the still hot test tube into a beaker containing about 20 ml of distilled water. The tube will break down and, if not, use a glass rode to break it. The resulting solution is heated almost to boiling and filtered. The filtrate, which should be colorless, is used for the specific tests.

To remove the excess unreacted sodium add a small quantity of alcohol (ethanol or methanol) to the test tube before breaking it with heating so that the alcohol will react with the excess sodium metals to give sodium alkoxide.



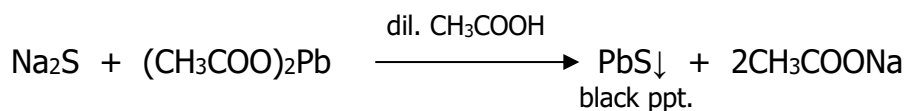
### 1- Detection of Nitrogen

To 3 ml of the filtrate add 4 drops (0.2 gm) of ferrous sulfate  $\text{FeSO}_4$  solution. Check the basicity of the solution and make it basic by the addition of enough sodium or potassium hydroxide solution (10%). Heat for boiling (30 second). Now add drops of dilute sulfuric acid enough to make the solution acidic. A Prussian blue precipitate indicates a positive test of nitrogen.

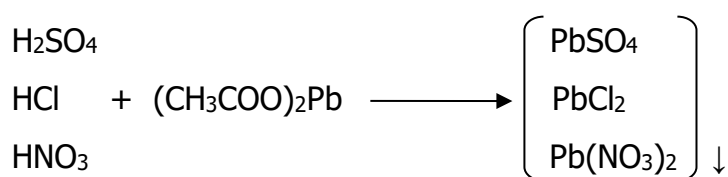


## 2- Detection of Sulfur

Acidify 2 ml of the filtrate with dilute acetic acid. Then add 5 drops of lead acetate solution. A black precipitate of lead sulfide indicates the presence of sulfur.

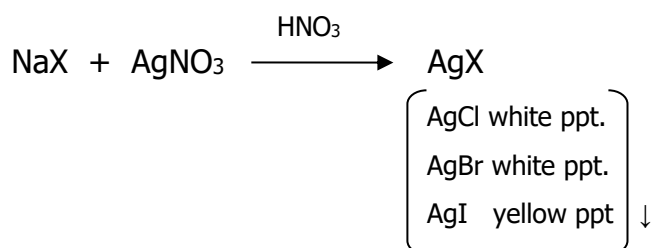


Acetic acid is used in the acidification and not other acids ( $\text{H}_2\text{SO}_4$ ,  $\text{HCl}$ ,  $\text{HNO}_3$ ) since they give insoluble white precipitate through reaction with lead acetate.

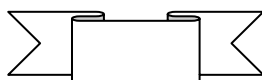
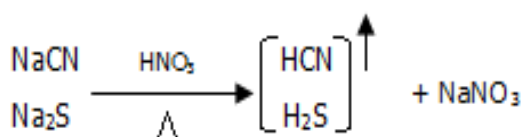


## 3- Detection of Halogens

In case of presence of nitrogen and sulfur in the compound, acidify 3 ml of the filtrate with dilute nitric acid (add drop by drop until the solution becomes acidic). Boil for 5 minutes and then add drops of silver nitrate. White or yellow precipitate indicates the presence of halogens.



Boiling for 5 minutes is done to remove nitrogen and sulfur present in the filtrate as hydrogen cyanide and hydrogen sulfide gases.



**Exp. 2****Qualitative Analysis of Organic Compounds**

Qualitative analysis of organic compounds helps identify and characterize unknown organic compounds. Many organic compounds are usually a component of a mixture of several compounds that might be considered as impurities. These impurities may be side products resulted during the preparation of the organic compound or may be decomposition products of the original pure organic compound and this occurs during storage under unsuitable conditions. On the other hand, some compounds may be obtained and stored pure because of their high degree of stability. In most cases a good separation and purification should precede qualitative analysis of organic compounds so that identification will be successful.

The qualitative analysis of any organic compound should follow these steps:

**A- Physical properties studying.**

- 1- State of the organic compound (solid, liquid, gas).
- 2- Determination of the melting point or boiling point.
- 3- Color, taste, and odor of the compound.
- 4- Determination of the solubility group (solubility classification according to the general families).

**B- Chemical properties studying.**

- 1- Effect of the compound or its solution on litmus paper.
- 2- Determination of elements in the organic compound (nitrogen, sulfur, or halogens).
- 3- Detecting of the organic groups, i.e. group classification to get more specific families.
- 4- Specific classification tests.
- 5- Preparation of derivatives.

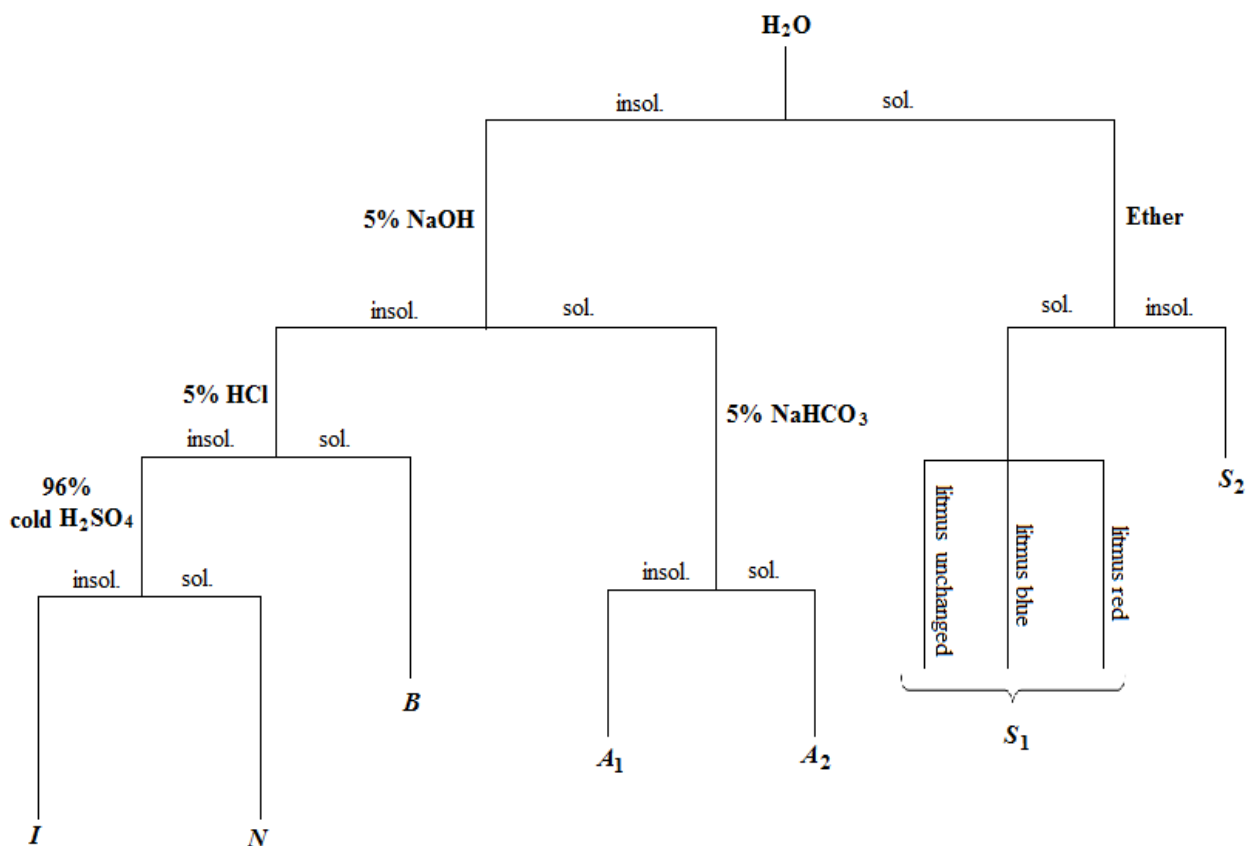
## Determination of Solubility Class

Solubility class determination gives an idea about the type of the functional group present in the compound, the polarity and molecular weight of the compound, and the nature of the compound (acidic, basic, neutral). This is accomplished by testing the solubility of the compound in either of the following sets of solvents: distilled water, 5% sodium hydroxide solution, 5% sodium bicarbonate solution, 5% hydrochloric acid solution, and cold concentrated sulfuric acid, or distilled water and ether.

It is well known that the hydrocarbons are insoluble in water because of their non polar nature. If an unknown compound is partially soluble in water, then this indicates that a polar functional group is present. Additionally, solubility in certain solvents often leads to more specific information about the functional group. For example, benzoic acid is insoluble in water, but is converted by 5% sodium hydroxide solution to a salt, sodium benzoate, which is readily water soluble. In this case, then, the solubility in 5% sodium hydroxide solution of a water insoluble unknown is a strong indication of an acidic functional group. Prediction of the molecular weight and size may sometimes be obtained from the result of solubility tests. For example, in many homologous series of monofunctional compounds, the members with fewer than about five carbon atoms are water soluble, whereas the higher homologs are insoluble.

The first step to follow is to test the solubility of the compound in water. Generally and for solubility classification purposes, the compound is said to be soluble in any solvent if it dissolves to the extent of about 3% (0.1 gm/3 ml or 0.2 ml/3 ml). This is achieved by dissolving about 0.1 gm of the solid compound or 3-4 drops of the liquid compound in gradually increasing volumes of the solvent up to 3 ml (max. allowed volume is 3 ml) with shaking. This technique is the one that should be followed in solubility classification to determine whether the compound is soluble or insoluble in that solvent.

When solubility in dilute acid or dilute base is being considered, the significant observation to be made is whether it is significantly more soluble in aqueous acid or aqueous base than in water. Such increased solubility is the desired positive test for acidic or basic functional groups. Below is very useful scheme for solubility classification.



## Solvents

### \* Water

Water is a polar solvent with a dielectric constant equals to 80. It has the ability to form hydrogen bonding and can act either as an acid or a base. Therefore it can dissolve:

- Salts of ammonium ion ( $\text{RNH}_4^+$ ) or organic acids salts with alkali metal cations ( $\text{RCOO}^-$ ).
- Ionic compounds.
- Polar compounds "like dissolve like"
- Organic compounds with low molecular weight (less than 5 carbon atoms) such as alcohols, aldehydes, ketones, and carboxylic acids.

Water is useful to determine the degree of acidity of a compound, even if the compound is insoluble in water, using litmus paper (acidic, basic, or neutral).

Water is the first solvent used to determine the solubility class of a compound. If the compound is water soluble, the next step is to test its solubility in ether.

### \* **Ether**

Ether is non-polar solvent having a dielectric constant of 4.3. It cannot form hydrogen bonding (unassociated liquid). Therefore, it differs from water in that it cannot dissolve ionic compounds such as salts. It dissolves most water insoluble compounds, therefore, in the determination of solubility class, the importance of ether is for water-soluble compounds only and no further solubility tests using the remaining solvents are to be done.

Accordingly two probabilities are there:

1- *Compounds soluble in both water and ether.*

These compounds:

- non ionic.
- contain five or less carbon atoms.
- contain an active group that is polar and can form hydrogen bonding.
- contain only one strong polar group.

This division of compounds is given **S<sub>1</sub>** class and includes, e.g., aldehydes, ketones, and aliphatic acids.

2- *Compounds soluble in water only (but not in ether).*

These compounds:

- ionic.
- contain two or more polar group with no more than four carbon atoms per each polar group.

This group is classified as **S<sub>2</sub>** class and includes ionic salts such as salts of carboxylic acids and amines and compounds with more than one active group such as poly hydroxylated compounds and carbohydrates.

Not that solubility in ether is tested only for water-soluble compounds. For water insoluble compounds use the left side of the solubility classification scheme, i. e. test solubility in sodium hydroxide rather than ether.

### \* 5% NaOH and 5% NaHCO<sub>3</sub>

Water insoluble compounds must be tested first in 5% sodium hydroxide solution which is a basic solvent. It reacts with water insoluble compounds that are capable of donating protons such as strong and weak acids. The stronger the acid, the weaker the base it can react with. Water insoluble compounds that dissolve in 5% sodium hydroxide solution must also be tested for solubility in 5% sodium bicarbonate solution. Therefore, for water insoluble acidic compounds sodium hydroxide solution is considered as a *detecting solvent* whereas sodium bicarbonate solution is called as a *sub classifying solvent* since it can react with strong acidic only. That is, these two solvents gives an idea about the acidity degree of the compound. Note that testing solubility in 5% sodium bicarbonate solution is not needed if the compound is insoluble in 5% sodium hydroxide solution, but rather, 5% hydrochloric acid solution should be used.

Two probabilities are there:

#### 1- *Compounds soluble in both bases.*

This group is given class **A<sub>1</sub>**. This class includes strong acids that have the ability to react with weak bases (carboxylic acids) and phenols with electron withdrawing groups (e. g., -NO<sub>2</sub>). Protons are weakly attached and can be given easily.

#### 2- *Compounds soluble in 5% sodium hydroxide solution only.*

This group is given class **A<sub>2</sub>** and it includes phenols, amides, and amino acids.

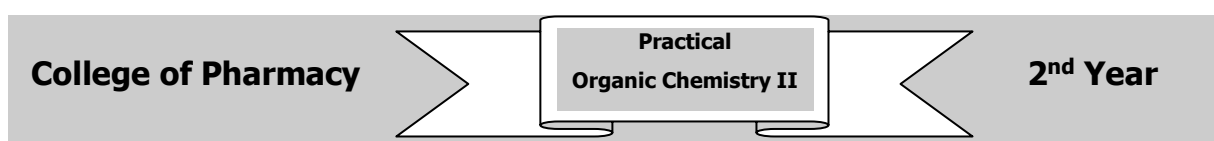
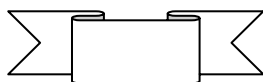
### \* 5% HCl

If the compound is insoluble in water and sodium hydroxide solution (and, hence, insoluble in sodium bicarbonate solution too), this means that the compound is not an acid but, rather, is either a basic compound or a neutral compound. 5% hydrochloric acid solution, which can dissolve basic compounds such as amines (RNH<sub>2</sub>), is used for such a compound. If the compound is soluble in this solvent, then it is given class **B**. This class include primary, secondary, and tertiary amines.

### \* Cold concentrated H<sub>2</sub>SO<sub>4</sub>



If the compound is insoluble in water, 5% sodium hydroxide solution, and 5% hydrochloric acid solution, solubility in cold concentrated sulfuric acid should be tested. If the compound is soluble in this acid, it belongs to class **N** which include neutral compounds such as high molecular weight alcohols, aldehydes, ketones, esters, and ethers, (more than four carbon atoms), and unsaturated hydrocarbons. On the other hand, compounds that are insoluble in cold concentrated sulfuric acid belong to class **I** which includes inert aliphatic hydrocarbons.



### Exp. 3

## Identification of Alkyl and Aryl Halides

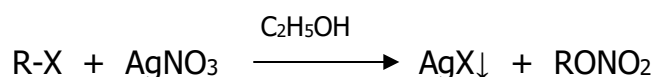
All alkyl halides and chlorobenzene are colorless liquids when pure except iodoform,  $\text{CHI}_3$ , which is a yellow crystalline solid with a characteristic odour. Methyl iodide, ethyl iodide and bromide, chloroform, and carbon tetrachloride have sweetish odours. Benzyl chloride has a sharp irritating odour and is lachrymatory. Chlorobenzene possesses aromatic odour.

Alkyl and aryl halides ( $\text{R-X}$ ,  $\text{Ar-X}$ ) have boiling points higher than the parent hydrocarbons because of the heavier molecular weight. Accordingly, for a given compound, iodides have the higher boiling point than bromides and chlorides.

In spite of their polarity alkyl halides are insoluble in water due to their inability to form hydrogen bonds. They are soluble in most organic solvents. Iodo-, bromo-, and polychloro- compounds are denser than water.

### 1- Reaction with alcoholic silver nitrate

Alcoholic silver nitrate reagent is useful in classifying halogen compounds. Many halogen containing compounds react with silver nitrate to give an insoluble silver halide ( $\text{AgX}$ ), and the rate of this reaction indicates the degree of reactivity of the halogen atom in the compound. Besides, the identity of the halogen can sometimes be determined from the color of the silver halides produced; silver chloride is white (turns to purple on exposure to light), silver bromide is pale yellow, and silver iodide is yellow. These should, of course, be consistent with result from elemental analysis (sodium fusion for detection of halogens).



### Procedure

Add one drop or a couple of crystals of the unknown to 2  $\text{cm}^3$  of 2% ethanolic silver nitrate solution. If no immediate reaction is observed, stand for 5 minutes at room temperature and observe the result. If no reaction takes place, warm the mixture in water bath for 30 seconds and observe any change. If there is any precipitate ( $\text{AgX}$ )

add several drops of 1 M nitric acid solution to it; silver halides are insoluble in this acid.

*tertiary* chlorides, methyl and ethyl iodides, and ethyl bromide give fast result at room temperature whereas *primary* and *secondary* chlorides, and benzyl chloride give result only on warming. Chlorobenzene, chloroform, iodoform and carbon tetrachloride don't give any positive result.

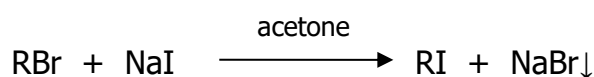
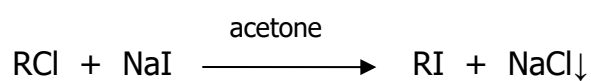
## 2- Sodium iodide in acetone test

This test, complementing the alcoholic silver nitrate test, is used to classify aliphatic chloride and bromide as primary, secondary, or tertiary. The test depends on the fact that sodium chloride and sodium bromide are only very slightly soluble in acetone.

The mechanism follows direct displacement ( $S_N2$ ) process; therefore, the order of reactivity of simple halides is:



With sodium iodide, primary bromides give a precipitate of sodium bromide within 3 minutes at 25°C, whereas the chlorides give no precipitate and must be heated to 50°C in order to effect a reaction. Secondary and tertiary bromides react at 50°C, but the tertiary chlorides fail to react within the time specified. Tertiary chlorides will react if the test solutions are allowed to stand for a day or two.



## Procedure

to 1 cm<sup>3</sup> of the sodium iodide-acetone reagent in a test tube add two drops of the compound. If the compound is a solid, dissolve about 0.1 gm in the smallest possible volume of acetone, and add the solution to the reagent. Shake the test tube, and allow the solution to stand at room temperature for 3 minutes. Note whether a precipitate

is formed and also whether the solution turns reddish brown, because of the liberation of free iodine. If no change occurs at room temperature, place the test tube in a water bath at 50°C. Excessive heating causes loss of acetone and precipitation of sodium iodide, which can lead to false-positive results. At the end of 6 minutes, cool to room temperature and note whether a reaction has occurred. Occasionally, a precipitate forms immediately after combination of the reagent; this represents a positive test only if the precipitate remains after the mixture is shaken and allowed to stand for 3 minutes.

### **3- Differentiation between alkyl and aryl halides**

#### **(Formaldehyde-sulfuric acid test)**

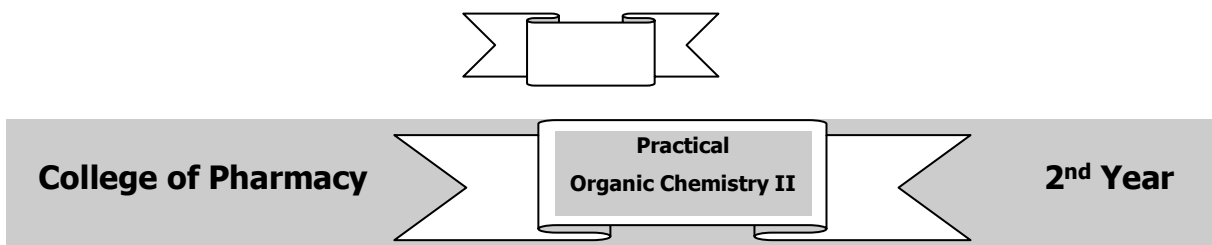
With this test aryl halides (chlorobenzene) produce pink, red, or bluish red color, whereas alkyl halides produce yellow, amber, or brown color.

#### **procedure**

This reagent is prepared at the time of use by adding 1 drop of formaldehyde to a test tube containing 1 cm<sup>3</sup> concentrated sulfuric acid. In another test tube add 1 drop of the compound to be tested to 1 cm<sup>3</sup> of hexane. From this solution take 1-2 drops and add them to 1 cm<sup>3</sup> of the reagent. Shake well and observe the color.

### **4- Reduction of Fehling's reagent (special tests for chloroform)**

Boil 1 cm<sup>3</sup> of chloroform gently (water bath) with 3 cm<sup>3</sup> of Fehling's reagent with constant shaking for 3-4 minutes. Reduction occurs and reddish cuprous oxide slightly separates.



#### **Exp. 4**

## Identification of Alcohols

All alcohols contain the hydroxyl group (-OH) attached to a saturated carbon. These have the general formula R-OH, where R is an alkyl or substituted alkyl group. The group may be primary, secondary, or tertiary; it may be open chain or cyclic; it may contain a double bond, a halogen atom, an aromatic ring, or additional hydroxyl group. The -OH group is the functional group, determines the properties characteristic of this family. Variations in structure of the R group may affect the rate at which the alcohol undergoes certain reactions, and even, in a few cases, may affect the kind of reaction.

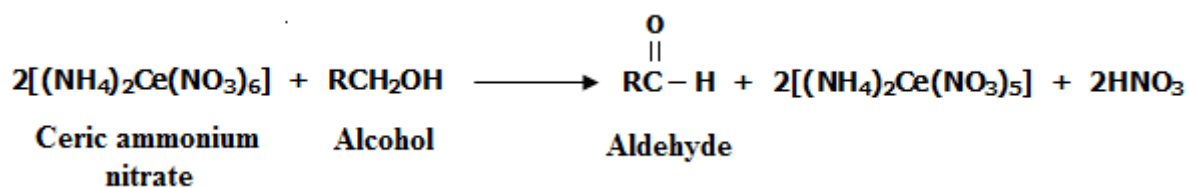
Alcohol molecules are polar, because the -OH group is highly polar. Force of attraction between alcohol molecules obviously must be greater than between molecules of alkanes. Hydrogen bonding account for this.

The presence of an alcohol group sharply increases the tendency to dissolve in water. Methane, for example, is insoluble in water, but methyl alcohol is completely soluble, because of the hydrogen bonding with water. Low molecular weight alcohols are soluble in water and ether are classified under class **S<sub>1</sub>** such as methanol and ethanol. Alcohols that are insoluble in water are related to class **N** such as benzyl alcohol, *sec*-butanol, and cyclohexanol.

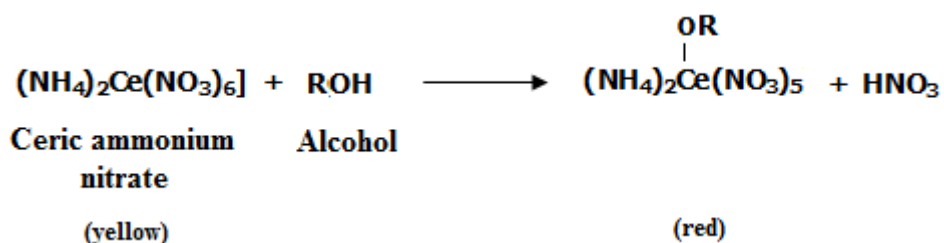
Alcohols are saturated compounds containing the functional group -OH. They can undergo nucleophilic substitution reactions, in which the hydroxyl group is displaced by other groups, or they can undergo elimination reactions, involving the loss of the elements of water when reacted with a dehydrating agent. Primary and secondary alcohols also undergo oxidation and the hydroxyl group shows acidic properties when treated with reactive metals.

### 1- Ceric ammonium nitrate test (general test)

Ceric ammonium nitrate (yellow solution) is an oxidizing agent that reacts with alcohols to give a red complex and with phenols to give a brown to greenish brown precipitate.



Each mole of the alcohol requires two moles of the reagent. The red complex is an intermediate for the oxidation of alcohols by the Ce(IV) solution. This red color disappears after a reasonable time due to completing the oxidation of this intermediate and the reduction to the colorless Ce(IV) solution producing the corresponding aldehyde or ketone.



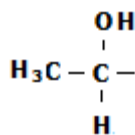
This test gives positive results with primary, secondary, and tertiary alcohols (up to 10 carbons), poly hydroxylated compounds such as carbohydrates, and hydroxylated carboxylic acids, aldehydes and ketones.

## Procedure

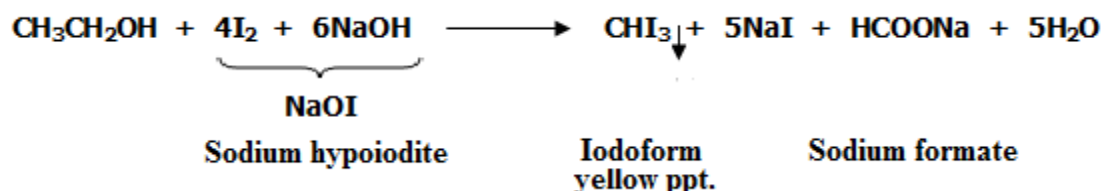
Mix 2 drops of the alcohol with 1 drop of ceric ammonium nitrate solution. A red complex indicates a positive test. If the alcohol is insoluble with water dissolve the two drops of alcohol with 0.5 cm<sup>3</sup> dioxane, shake well, and add one 1 drop of the reagent.

## 2- Iodoform test

This test is specific for alcohols which have a free methyl group and a hydrogen attached to the carbon bearing the hydroxyl group such as ethanol and *sec*-butanol.



The overall reaction is:



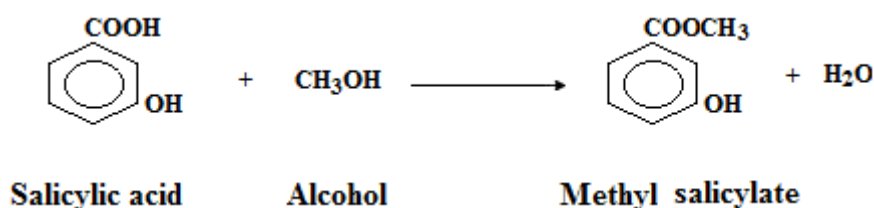
The alcohol is oxidized to the corresponding aldehyde or ketone by the action of the oxidizing agent 'sodium hypoiodite' which also cause the aldehyde or ketone to be tri-iodinated on the terminal methyl group producing iodoform as a yellow precipitate.

## Procedure

To 0.2 cm<sup>3</sup> of alcohol add 2 cm<sup>3</sup> distilled water (or 2 cm<sup>3</sup> dioxane for water insoluble compounds), add about 1cm<sup>3</sup> of 10% sodium hydroxide solution, then add iodine solution drop wise with shaking until either a yellow iodoform precipitate is produced (or add 2 cm<sup>3</sup> of 0.5 M potassium iodide solution and 4 cm<sup>3</sup> sodium hypochlorite solution). Warm the mixture to 50°C for 2 minutes in a water bath, and then cool it. If the alcohol is ethanol or *sec*-butanol, fine yellow crystals of iodoform (Triiodomethane) are produced.

## 3- Salicylic acid test

When salicylic acid reacts with methanol, methyl salicylate is formed, and the smell of it is very distinguishable.



## Procedure

Heat 1 cm<sup>3</sup> of (methanol) with spatula load of salicylic acid and a few drops of conc. H<sub>2</sub>SO<sub>4</sub> for 1 minute. Cool and pour the mixture into about 10 cm<sup>3</sup> of distilled water in a small beaker and note the smell of methyl salicylate.

## 4- Acetic acid test

Ethanol can be confirmed by reaction with glacial acetic acid. Ethyl acetate (ethanoate) is formed, and the smell of it is distinguishable.

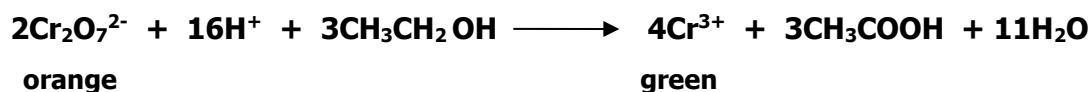


## Procedure

put 1 cm<sup>3</sup> of the substance into a test-tube then adding 1 cm<sup>3</sup> of glacial acetic acid and a few drops of conc. H<sub>2</sub>SO<sub>4</sub>. Heat the tube for one minute and then pour the mixture into about 10 cm<sup>3</sup> of water in a small beaker. The fruity odour of ethyl acetate (ethanoate) should be apparent.

## 5- Potassium dichromate test

When ethanol is reacted with potassium dichromate in the presence of conc. H<sub>2</sub>SO<sub>4</sub>, acetaldehyde (ethanol) is formed and it is replaced acetic acid.



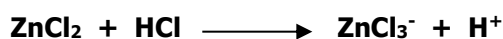
## Procedure

Make up 4 cm<sup>3</sup> of a concentrated solution of potassium dichromate and add 1 cm<sup>3</sup> of conc. H<sub>2</sub>SO<sub>4</sub>. Warm the mixture gently and then add 0.5 cm<sup>3</sup> of ethanol: the sweet smell of acetaldehyde should become apparent and it is replaced by the sharp smell of acetic acid.

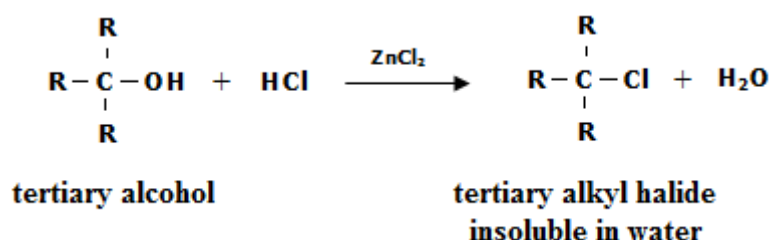
## 5- The Lucas test



This is done to distinguish between primary, secondary and tertiary alcohols. It depends on the formation of alkyl chloride as a second liquid phase. Lucas reagent is zinc chloride dissolved in conc. HCl. Zinc chloride is added to increase the ionization of hydrochloric acid.



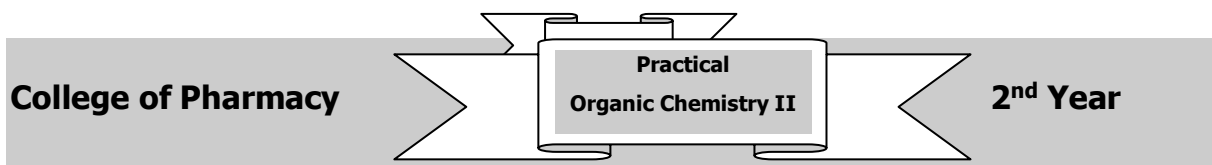
Benzyl alcohol gives the fastest positive result. Tertiary alcohols are faster in the formation of conjugated halides than secondary alcohols. Primary alcohols don't form two layers.



## Procedure

Put 1 cm<sup>3</sup> of the alcohol into a test-tube. Add 6 cm<sup>3</sup> of Lucas reagent, cork the test-tube and shake it. Allow it to stand for five minutes.

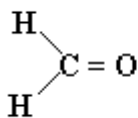
With primary alcohol of low relative mass, the aqueous layer remains clear, with secondary alcohols, chlorides separate on standing for 15-20 minutes, with tertiary alcohols separation takes place immediately.



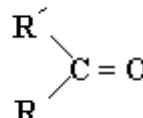
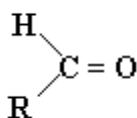
## Exp. 5

## Identification of Aldehydes and Ketones

Aldehydes are compounds of the general formula **RCHO**, ketones are compounds of the general formula **RR'CO**. The groups R and R' may be aliphatic or aromatic. (In one aldehyde, HCHO, R is H).



**Aldehydes**



**Ketone**

Both aldehydes and ketones contain the carbonyl group C=O, and are often referred to collectively as carbonyl compounds. It is the carbonyl (the functional group) that largely determines the chemistry of aldehydes and ketones.

It is not surprising to find that aldehydes and ketones resemble each other closely in most of their properties. However, there is a hydrogen atom attached to the carbonyl group of aldehyde, and there are two organic groups attached to the carbonyl group of ketones. This difference in structure affects their properties in two ways: (a) aldehydes are quite easily oxidized, whereas ketones are oxidized only with difficulty; (b) aldehydes are usually more reactive than ketones toward nucleophilic addition, the characteristic reaction of carbonyl compounds.

The polar carbonyl group makes aldehydes and ketones polar compounds, and hence they have higher boiling points than non-polar compounds of comparable molecular weight. By themselves, they are not capable of intermolecular hydrogen bonding since they contain hydrogen bonded only to carbon, as a result they have lower boiling points than comparable alcohols or carboxylic acids.

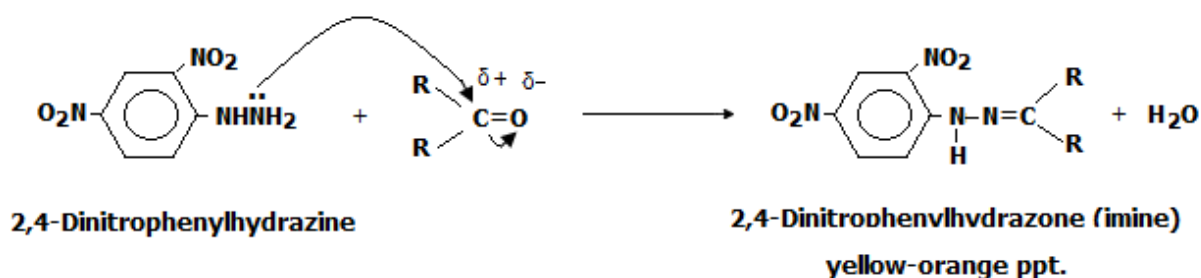
The lower aldehydes and ketones are appreciably soluble in water, presumably because of hydrogen bonding between solute and solvent molecules; borderline solubility is reached at about five carbons. Aldehydes and ketones are soluble in the usual organic solvents.

In a carbon-carbon double bond C=C, both the  $\sigma$ - and  $\pi$ -electron clouds are symmetrically distributed between the two carbon atoms. In the carbon-oxygen double bond (i.e. carbonyl group) C=O, both the  $\sigma$ - and  $\pi$ -bonds are polarized, the electrons being distributed unequally between the two atoms. Owing to the greater

electronegativity of the oxygen atom, this atom has the greater share of the bonding electrons and the distortion of the  $\pi$ -electron density can be represented in several ways. As a result of the permanent polarization of the bond, the carbon atom is electrophilic in character and is therefore susceptible to nucleophilic attack, i. e. attack by reagents which are able to donate an electron-pair to the carbon atom and form new bond. Conversely, the oxygen atom is susceptible to electrophilic attack, i. e. attack by an electron-pair acceptor, but this usually involves the comparatively simple step of protonation (i. e. reaction with  $H^+$ ).

### 1- (2,4-Dinitrophenylhydrazine) test (general test)

Both aldehydes and ketones give yellow or orange precipitate with 2,4-Dinitrophenylhydrazine reagent.

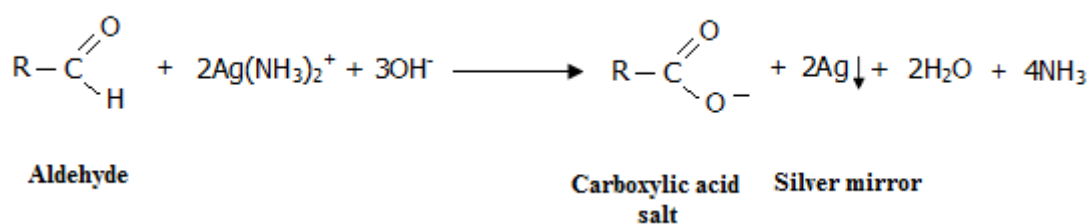


### Procedure

To 2 drops of the compound add 3 drops of the reagent, a yellow or orange precipitate will be formed. If the compound is insoluble in water, dissolve it in  $1\text{ cm}^3$  of methanol and then add the reagent.

### 2- Tollen's test

All aldehydes reduce ammonium silver oxide (Tollens reagent), and oxidize to carboxylic acids, while ketones cannot be oxidized, they need stronger oxidizing agents. Tollen's reagent is the combination of silver nitrate solution with ammonium hydroxide in the presence of sodium hydroxide solution. Silver ions reduced from this reagent to silver element in the form of silver mirror on the inner side of the test tube.



## Procedure

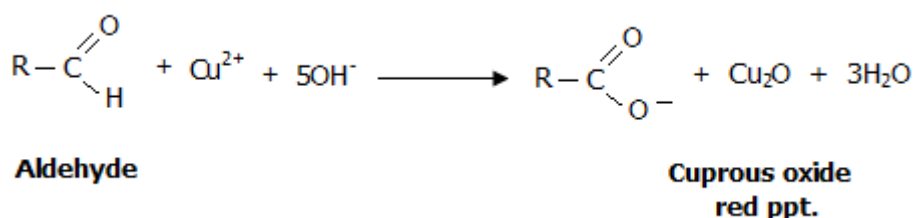
To prepare Tollen's reagent add 2-3 drops of 10% sodium hydroxide solution to 3 cm<sup>3</sup> of 5% silver nitrate solution, and then add drop wise 10% ammonia solution with continuous shaking until all the brown precipitate of silver oxide is dissolved. This reagent should be freshly prepared.

In a test-tubes put 2 cm<sup>3</sup> of Tollen's reagent, then add few drops of the compound. Silver mirror will be formed on the walls of the test-tubes. (If silver does not precipitate, heat for a while on a water bath. The excessive heating will cause of appearance of a false positive test by decomposition of the reagent.

The formed silver mirror can be washed using dilute nitric acid. If the test tube is not very clean, silver metal forms merely as a granular gray or black precipitate. False negative tests are common with water insoluble aldehydes. A negative result indicates that the compound is a ketone.

## 3- Fehling's test

This test, like Tollen's test, is used to distinguish aldehydes from ketones. Only aldehydes can reduce Fehling's reagent (blue solution) and give red precipitate, due to the reduction of Cu<sup>2+</sup> to Cu<sup>1+</sup>. The red product is cuprous oxide Cu<sub>2</sub>O.



Aromatic aldehydes do not give this test because of their sensitivity toward basic media.

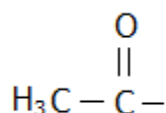
## Procedure

Fehling's A solution is an aqueous solution of copper sulfate ( $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ ) with few drops of conc.  $\text{H}_2\text{SO}_4$ , whereas Fehling's B solution is an aqueous solution of potassium sodium tartrate ( $\text{C}_4\text{H}_4\text{KNaO}_6 \cdot 4\text{H}_2\text{O}$ ) and sodium hydroxide.

In a test-tube put  $3 \text{ cm}^3$  of the compound, then add 1 ml Fehling A and 1 ml Fehling B, then heat the test-tube for 5 minutes. The blue color of the mixture changes to red. Ketones don't change the color of this reagent.

## 4- Iodoform test

This test special for aldehydes and ketones containing a terminal methyl group:



These compounds include acetaldehyde, acetone, acetophenone, and benzyl methyl ketone. All of them have a methyl group attached to the carbonyl group.

## Procedure

To  $0.2 \text{ cm}^3$  of compound add  $2 \text{ cm}^3$  distilled water (or  $2 \text{ cm}^3$  dioxane for water insoluble compounds), add about  $1 \text{ cm}^3$  of 10% sodium hydroxide solution, then add iodine solution drop wise with shaking until either a yellow iodoform precipitate is produced (or add  $2 \text{ cm}^3$  of 0.5 M potassium iodide solution and  $4 \text{ cm}^3$  sodium hypochlorite solution). Warm the mixture to  $50^\circ\text{C}$  for 2 minutes in a water bath, and then cool it. A yellow crystals of iodoform (Triiodomethane) are produced.

## 5- Sodium nitroprusside $\text{Na}_2[\text{Fe}(\text{CN})_5\text{NO}]$ test

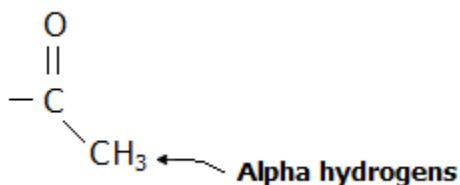
This test is also special for aldehydes and ketones containing a terminal methyl group.

## Procedure

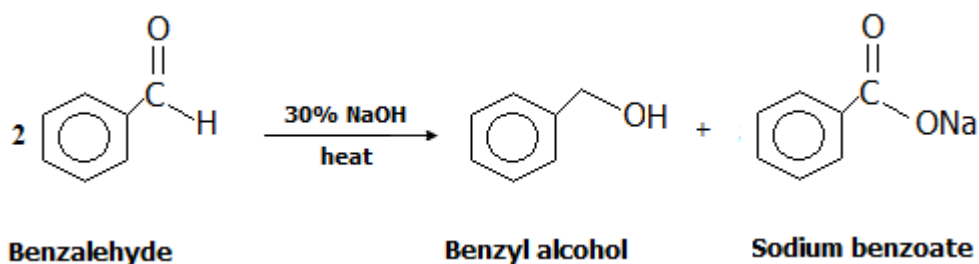
In a test-tube put  $1 \text{ cm}^3$  of the compound, then add  $1 \text{ cm}^3$  of 5% sodium nitroprusside  $\text{Na}_2[\text{Fe}(\text{CN})_5\text{NO}] \cdot 2\text{H}_2\text{O}$  solution, then add a drops of 30% NaOH solution. The result is red color.

## 6- Cannizzaro reaction

Benzaldehyde, salicylaldehyde, and formaldehyde can undergo Cannizzaro reaction because they do not have alpha hydrogen atom.



In this type of reactions the aldehyde undergoes a self oxidation-reduction in the presence of a strong basic medium to yield a mixture of the corresponding alcohol and the salt of the corresponding carboxylic acid (or the acid itself). Therefore, one molecule of the aldehyde serves as the oxidizing agent while the other serves as the reducing agent.



### Procedure

Put in a test-tube 1 ml Benzaldehyde, and then add few drops 30% NaOH, and heat gently on a water bath with shaking for few minutes. A precipitate of sodium benzoate is produced. Dissolve this precipitate by adding few drops of distilled water, and then add drops of concentrated hydrochloric acid to liberate benzoic acid as a white precipitate.

Put in a test-tube 1 cm<sup>3</sup> acetaldehyde, then add few drops 30% NaOH solution. Yellow plastic material will be formed its color change to brown with time, and does not dissolve in water.

Formaldehyde can undergo this reaction, however, this reaction can't be relied on for testing formaldehyde since the acid produced, formic acid, is liquid that can't be observed separately as compared to the solid benzoic acid resulted from benzaldehyde.

