Practical Organic Chemistry for First Year biology and Biotechnology Students

م. د. عمر عبد اللطيف محمد
أ. م.د ختام طارق احمد
ا. م. د. عدي هادي رؤوف
م. سرور عبد الرحمن مهدي
م. م. ساحل عبد الحسين

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Exp: (1)

DETERMINATION OF MELTING POINT

The Melting Point of a solid crystalline compound is the temperature at which the solid begins to change into liquid under a pressure of one atmosphere, or it is the temperature at which there is equilibrium between liquid and solid states. If the resultant liquid is cooled, solidification will occur at the same temperature, *i.e.* the melting point and the freezing point for a pure substance are identical/ The melting point is considered as a criterion of purity of a compound and is useful for identification of organic compounds.

There is a temperature difference between the beginning of melting (T_1) and the end of melting (T_2) at which the entire solid converts into liquid (*The Melting Point Range*).

Pure organic compounds usually have sharp melting points and they melt within a range of about 0.5-1 °C, while impure substances have no sharp melting points and melt over a range of several degrees. The same idea will apply for pure organic compounds if they undergo slight decomposition before reaching the melting point .The decomposition products act as impurities that decrease the melting point and increase the melting point range.

Mixed Melting Point

Suppose that you have two solid samples (A and B) with the same melting point. If you do not know whether these two samples are the same or different, you can mix them and measure the melting point for the resultant mixture. If A and B are different, one of them will act as an impurity for the other and the measured melting point will be lower than the original one with a higher melting point range. On the other hand, if the measured melting point is the same as the original one, A and B represent the same compound.

Procedure

The method used for the determination of the melting point is called the Capillary Tube Method.

Few milligrams of the solid are placed in a thin glass capillary tube having a diameter of about 1 mm. The capillary tube is attached to a thermometer (by a rubber ring) in such a way that its closed end is attached to the bottom of the thermometer's bulb. Then both of them are placed in an oil bath (the rubber ring should be above the surface of the oil bath). Heating is started gradually.

The range between the temperature at which the powdered solid inside the capillary tube begins to liquefy (T_1) and the temperature at which a clear liquid is observed inside the capillary tube (T_2) is recorded as the observed melting point range.

Notes:

- The solid compound must be finely powdered.
- The temperature of the oil bath, paraffin or glycerin, should rise very slowly. Therefore, gentle heating and continuous stirring are necessary.
- The capillary tube containing the powdered solid substance is attached to the thermometer by a small rubber ring.
- After completing the experiment the oil liquid must be allowed to cool before using it again.

Exp: (2)

DETERMINATION OF BOILING POINT

The Boiling Point of an organic liquid is the temperature at which its vapour pressure equals the atmospheric pressure over the liquid, or it is the temperature at which the vapour and liquid phases are in equilibrium at a given pressure. The boiling point is considered as a criterion of purity of a compound and is useful for identification of organic compounds.

Similar to the melting point the boiling point may be sharp or may vary over a temperature range. Pure liquids have sharp boiling points while mixtures show a boiling point range.

The atmospheric pressure plays an important role in determination of the boiling point correctly. Reduction of the pressure leads to a decrease or a depression in the boiling point and vice versa.

procedure

1-A 5-cm capillary tube closed from one end is inverted upside down and put in a test tube containing a small quantity of liquid whose boiling point is to be measured.

2-The test tube is attached to iron stand by a clamp and placed in water bath.

3-The thermometer is attached to iron stand by a clamp and placed in water bath.

4- Start heating with continuous stirring until a rapid stream of bubbles comes out of the capillary tube (inside the liquid).

5-Remove the flame and allow the oil bath to cool so that the bubble stream will become slower and slower as the temperature drops until a point is reached at which bubbling ceases and the liquid starts to raise inside the capillary tube.

6-Record this temperature as the boiling point.

Exp: 3

RECRYSTALLIZATION

Solid organic compounds when isolated from organic reactions are usually impure; they are usually contaminated with small amounts of other compounds that are produced along with the desired compound. The purification of impure crystalline compounds is usually done by recrystallization from a suitable solvent or a mixture of solvents.

The purification of solids by crystallization is based upon differences in their solubility in a given solvent or a mixture of solvents.

Choosing a Solvent for Recrystallization

The proper choice of a solvent is an important part of the art of crystallization.

The ideal solvent should:

1. be chemically inert toward the solute.
2. dissolve the solute readily at its boiling point but sparingly at low temperatures (0 – 25 °C).
3. dissolve impurities either very easily or not at all.
4. not be flammable, of low cost, and of low toxicity.

Practically, to choose a good solvent take about 0.1 gm of the compound to be purified (a pure sample) and try to dissolve it in 1 ml of the solvent: if it dissolves in the cold solvent, the solvent will not be good for recrystallization; if it dissolves in the solvent with heating, the solvent will be good for recrystallization: if it does not dissolve in the solvent even with heating, the solvent will not be good for recrystallization. Solvents extensively used for recrystallization include water, ethanol, chloroform, ether, acetone, and benzene.

Decolourizing Charcoal

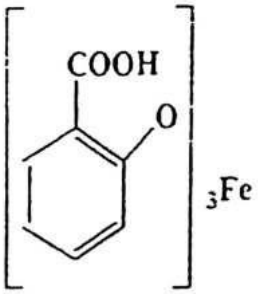
Frequently, samples to be purified may contain soluble coloured impurities that may cause the solution and the crystals to be coloured when they should be colourless: they dissolve in the boiling solvent and are adsorbed on the crystals produced upon cooling.

These impurities can be removed by treating the coloured sample with decolourizing (activated) charcoal that is composed of fine carbon particles with a large active surface on which the coloured impurities will be adsorbed.

Charcoal is added to the hot solution before boiling and the solution is kept hot at or near the boiling point for about 3–5 minutes with shaking to wet the charcoal. The solution is then filtered through a fluted filter paper. No more charcoal than actually needed should be used because any excess amount will cause the desired compound to be adsorbed on the charcoal.

Charcoal is not added at the boiling point of the solvent because its particles function as thousands of boiling chips causing the solution to boil over and foam.

Charcoal is not used in the recrystallization of phenolic compounds (Ar–OH) because it contains ferric ions that, on heating the solution for some time, can react with the phenolic hydroxyls forming red coloured complexes, thus impairing the purification process.



violet complex

Recrystallization Using Mixed Solvents

This is applied when our compound is readily soluble in a solvent at room temperature, and at the same time is not soluble in another solvent. The two solvents must be completely miscible with each other such as alcohol and water, ether and pentane, and glacial acetic acid and water.

So the compound is dissolved in the solvent that it is soluble in, charcoal is used if required, and the solution is filtered to get rid of the insoluble impurities. Then the other solvent (in which the compound is insoluble) is added to the filtrate gradually until turbidity appears. The mixture is then left aside to facilitate crystallization

procedure

1-Take 1 gm. of impure benzoic acid and added a small quantity of charcoal.

2- Start dissolving in (30 ml.) of water and heating in Bunsen burner.

3- Filter the mixture while being hot.

4-Leave the filtrate to cool at room temperature to induce crystallization.

5-Filterthe mixture in Buchner (Buchner funnel, Buchner flask, section pump)

6-Observe the produced crystal.

7-Weight the sample after drying.

8-Calculate percentage%.

Weight of crude benzoic acid=

Weight of filter paper=

Weight of pure crystal=

Weight of pure crystal with filter paper_ Weight of filter paper

$$\%\text{yeild}=\frac{\text{weight of Pure crystal}}{\text{weight of crude benzoic acid}}\text{X}100$$

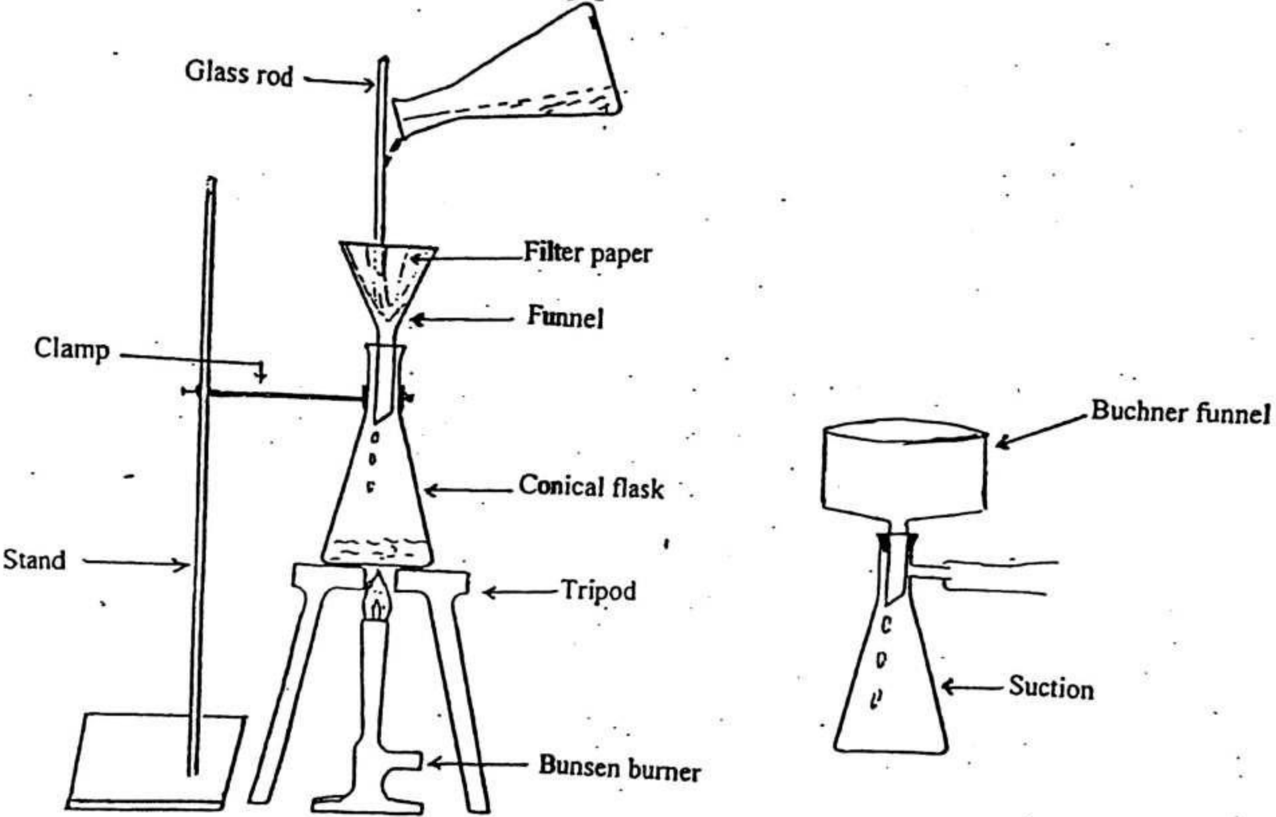
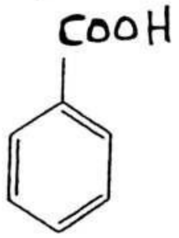


Fig. (2)

Question

1- why we used short stem funnel instead of a long stem funnel ?
2- why use the fluted filter paper in first filtration ?
3- What is the purpose of first filtration and second filtration?
4- Why we use conical flask(not beaker) in first filtration?
5- Why use (Buchner funnel, Buchner flask, section pump) in second filtration?
6- Why we don't add charcoal through the boiling point of the solution?



Benzoic acid

Notes

- If crystallization does not take place scratch the sides or the bottom of the container below the surface of the solution with a glass rod, add a small crystal of the pure compound. or evaporate some of solvent to induce the crystallization process.
- The funnel, filter paper, and the container of the solution should be kept hot through out the filtration process to prevent the deposition of the crystals on the filter paper or on the neck of funnel. Therefore, it is recommended to wash the filter paper after completing the filtration process with a small amount of the hot solvent.
- Use a minimum volume of the solvent to prevent the loss of the compound because large volumes of the solvent will keep most of the compound dissolved in it.
- Drying of the purified substance can be achieved by air drying, oven drying, freeze drying, or using a desiccator containing a drying agent such as anhydrous calcium chloride.

Boiling stones (boiling chips): are used to prevent local super heating, which intern cause bumping. Since the tiny air bubbles trapped in the pores of these stones provide nuclei for bubble formation that prevents local super heating.

EX(4) Simple distillation

EX(5) Fractional distillation

DISTILLATION

Distillation is a process of purification of liquid organic compounds by conversion to the vapour state with the aid of heat, and condensation of the vapours to the liquid state..

The temperature at which the liquid distills is a definite value (at a given pressure) for every pure organic compound and is known as the boiling point[1].

Aim of the Experiment

1. Purification of liquid organic substances.
2. Determination of the boiling point.
3. Separation of liquid organic substances from each other or from a non–volatile solid compound.

Distillation is limited to a certain extent because some organic compounds decompose when an attempt is made to distill them at a normal atmospheric pressure.

Types of Distillation

1. Simple distillation.

   This method is used for the separation of liquids having boiling points ranging from 30 °C to 150 °C and are stable to heat.

2. Vacuum distillation (distillation under reduced or diminished pressure).

   This method is used for the separation of liquids with high boiling points or are unstable to heat. These difficulties may be overcome by lowering the pressure over the substance, thus lowering the boiling point and the temperature necessary to effect the distillation (diminished–pressure distillation).

3. Steam distillation.

   This method is used for the purification of non–volatile organic compounds and which are immiscible with water.

4. Reflux distillation.

   This method is used to keep or prevent the reactants from loss by evaporation during a reaction.

5- Fractional distillation.

   This method is used for the separation of two or more liquids with different boiling points.

Fractional Distillation is the process of collecting separate fractions according to controlled boiling ranges during the distillation of a mixture of substances.

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[1] refer to experiment 2 page 5

Azeotropic mixture is a mixture composed of two or more liquids that form a constant–boiling mixture that boils at a certain temperature. It is impossible to separate them by fractional distillation. For example, a mixture of approximately 95% ethyl alcohol and 5% water produces a constant–boiling mixture (azeotropic mixture) which boils at 78.15 ℃.

Other examples of azeotropic mixtures include:

- benzene and ethanol
- carbon tetrachloride and methanol
- aniline and phenol
- formic acid and water
- toluene and acetic acid
- ethanol, benzene, and water

Procedure (for simple distillation)

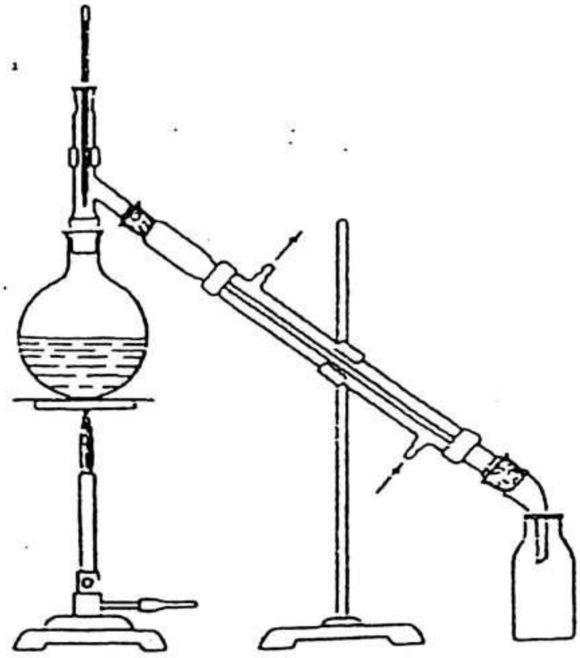
1. Put 100 ml of (water + $KMnO_4$) in the boiling Flask
2. Add 2-3 pieces of boiling chips.
3. Start the water running slowly through the condenser.
4. Heat until boiling.
5. Adjust the temperature so that distillation proceeds at 2-3 drops per second. Discard the first 2-3 ml of the distillate.
6. Continue distillation until you collect 30-60 ml.
7. Record the boiling point of your liquid, ethanol.

Discussion– Useful Notes

- Pure compounds distill over a very narrow range of temperatures.
- The boiling point is affected by impurities; some may increase the boiling point, others may decrease it, and some may not affect it. For example the addition of sodium chloride to water results in raising the boiling point of water. The effect observed here is the lowering of the vapour pressure of water; that is, the tendency of the molecules to escape has been diminished.
- Usually the first few milliliters contain water or volatile impurities, the second portion contains the pure substance.

Procedure : For (Fractional distillation)

1. Put 20 ml (10ml water + 10mL Ethanol) in the boiling flask
2. Add 2-3 pieces of boiling chips.
3. Start the water running slowly through the condenser.
4. Heat until boiling.
5. Adjust the temperature so that distillation proceeds at 2-3 drops per second. Discard the first 2-3 ml of the distillate.
6. Continue distillation until you collect 8-9 ml.
7. Record the boiling point of your liquid, ethanol.

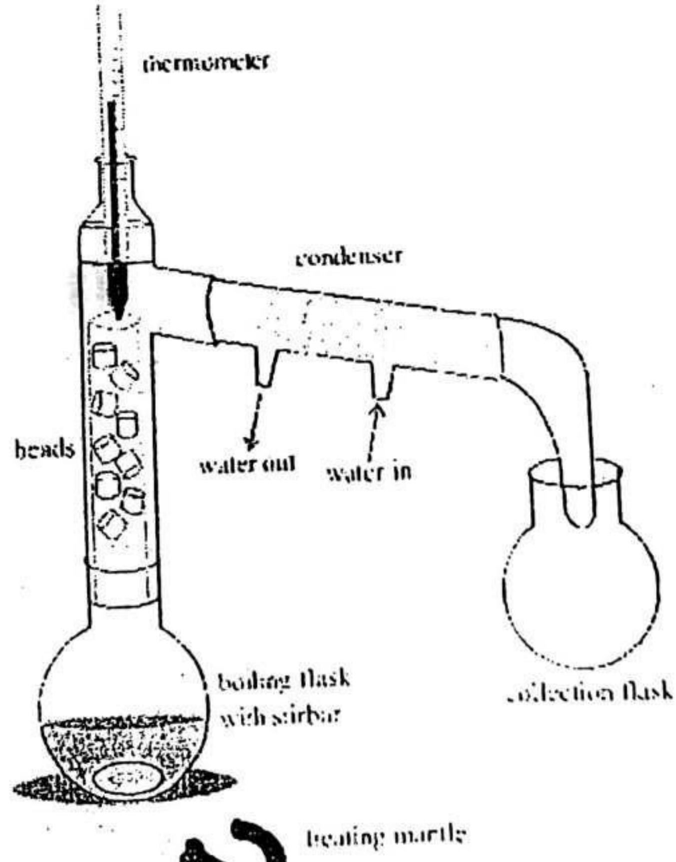


distillation apparatus assembly[2]

simple dis.

Questions

1. Explain why the first vapour in the distillation of two simple substances differs in composition from that of the original mixture.
2. How can you overcome the problem of decomposition of certain organic liquids during distillation process?



[distillation apparatus Fractional dis.]

EXPERIMENT (6)

The Functional Groups

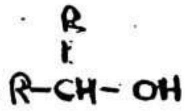
I-Alcohols

Alcohols are compounds of the general formula ROH , where R is any alkyl group ,it may contain a double bond or an aromatic ring .

Compounds in which the hydroxyl group is attached directly to an aromatic ring are not alcohols, they are (phenols). As the functional group of alcohols ,the Hydroxyl group (-OH) determines the properties characteristics of the family ,variations in the structure of the R group bring about variations in theses properties .Alcohols are classified as primary ,secondary or tertiary according to the kind of carbon that bears the -OH group

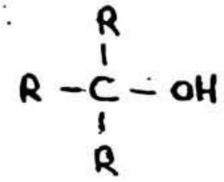
$R-CH_2-OH$

Primary alcohol (1°)



$R-\overset{R}{\overset{|}{C}}H-OH$

Secondary alcohol (2°)



$R-\underset{R}{\underset{|}{\overset{R}{\overset{|}{C}}}}-OH$

Tertiary alcohol(3°)

Experimental Part

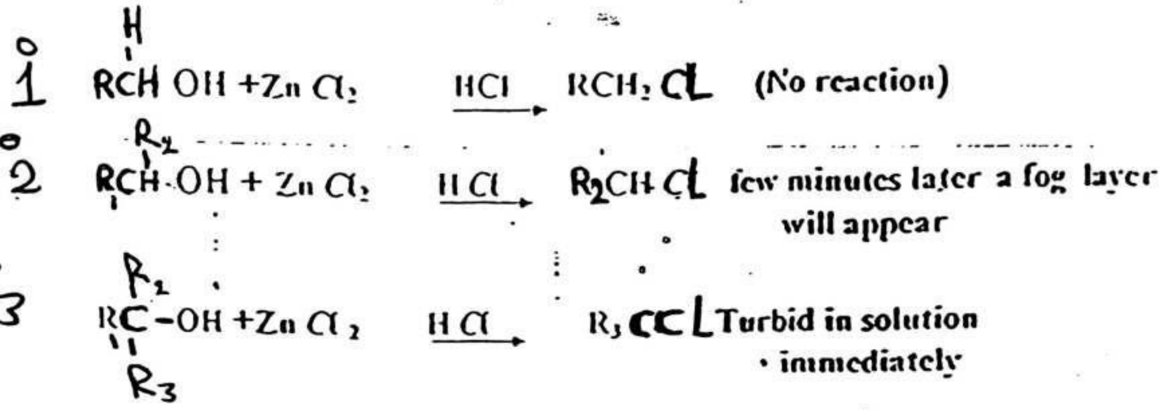
1-The general detection : the characteristic reagent for Hydroxyl group in alcohol is ceric ammonium nitrate $(NH_4)_2Ce(NO_3)_6$

Add few drops of ceric ammonium nitrate on (10 drops) of each type of alcohols (3°, 2°, 1°) gives dark red complex that refer to presence of alcohol.

$$RCH_2OH + (NH_4)_2Ce(NO_3)_6 \longrightarrow \underbrace{RCH_2\dot{O} + (NH_4)_2Ce(NO_3)_5}_{\text{dark red complexe}} + HNO_3$$

$$RCH_2\dot{O} + (NH_4)_2Ce(NO_3)_6 \longrightarrow RCHO + (NH_4)_2Ce(NO_3)_5 + HNO_3$$

[illegible]. The distinguish among three types of alcohol by using Lucas reagent ($ZnCl_2/HCl$) which is zinc chloride dissolved in concentrated hydrochloric acid. Take three test tubes, and put (3 drops) of each type of alcohols ($3^\circ, 2^\circ, 1^\circ$), then add (3 drops) of Lucas reagent and note the results, a fog layer of corresponding alkyl halide will appear.



1° $R\overset{H}{C}H\,OH + ZnCl_2 \xrightarrow{HCl} RCH_2Cl$ (No reaction)

2° $R\overset{R_2}{C}H\text{-}OH + ZnCl_2 \xrightarrow{HCl} R_2CHCl$ few minutes later a fog layer will appear

3° $R\overset{R_2}{\underset{R_3}{C}}-OH + ZnCl_2 \xrightarrow{HCl} R_3CCl$ Turbid in solution immediately

II-Alkyl Halides :

They are organic compounds that have general formula RX, **–X** is the halogen atom (Cl, Br, I), and R is an alkyl or substituted alkyl group while h\the compounds containing halogen attached directly to aromatic ring are called (*Aryl Halides*). 

The characteristic feature of the alkyl halide is the halogen atom –X, and the characteristic reaction of an alkyl halide are thos that take place at the halogen atom.

Inspite of their modes molarity, alkyl halides are insoluble in water, probably because of their inability to form hydrogen bonds. They are soluble in the organic solvents. Alky halides are prepared by different methods and nearly always prepared from alcohols. Alkyl halides enter nucleophilic substitution reaction (SN1, SN2), and Elimination reaction.

General detection

Where the alkyl halides enter substitution reactions ,they are react with alcoholic silver nitrate (alc.$AgNO_3$) to give white , palish yellow ,or dark yellow precipitate depending on the type of halogen attached to an alkyl group .

$$R-X + \underset{alc.}{AgNO_3} \longrightarrow AgX + R(NO_3)$$

X= Cl(white precipitated)
X =Br (palish yellow precipitated)
X=I(dark yellow precipitated)

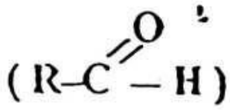
Alkyl halide characterized from Aryl halide that it gives positive detection with alc .$AgNO_3$.

$$R-X + \underset{(alc.)}{AgNO_3} \longrightarrow AgX\downarrow$$ Precipitate with alkyl halide

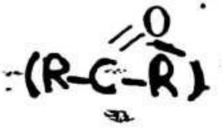
$$Ar-X + \underset{(alc.)}{AgNO_3} \longrightarrow N.R$$ No reaction with aryl halide

✓

III-Aldehydes and ketones



$(R-\overset{\overset{O}{\|}}{C}-H)$



$(R-\overset{\overset{O}{\|}}{C}-R`)$

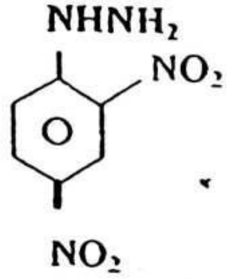
Aldehydes are compounds of the general formula $(R-\overset{\overset{O}{\|}}{C}-H)$; ketones are compounds of the general formula $(R-\overset{\overset{O}{\|}}{C}-R`)$ The groups **R** and **R`** may be aliphatic or aromatic (

both aldehyde and ketones contain the carbonyl group $C=O$. The carbonyl group is determined largely ,the chemistry of aldehyde and ketone.

Experimental Part

General detection

1 (2,4-dinitro phenyl hydrazine)

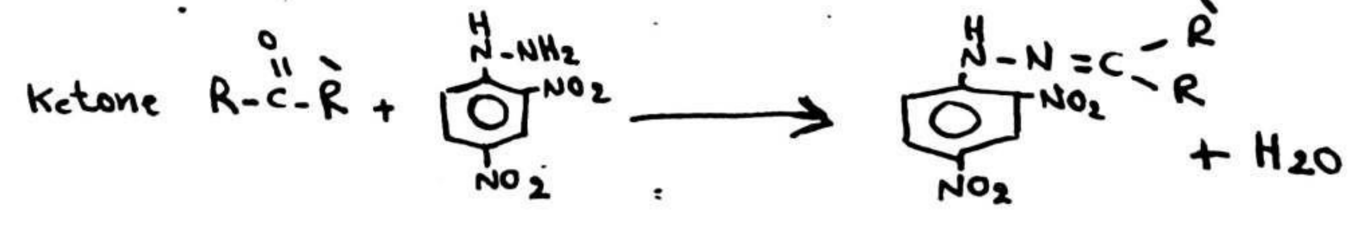


This reagent is characterized for carbonyl group in the aldehydes and ketones.

Add some drops from (2;4-dinitro phenyl hydrazine) to (3 drops of aldehyde and ketone ,gives yellow or orange precipitated, this refers to presence of carbonyl group .

2,4-dinitro hydrazine

2,4-dinitro phenyl hydrazone



2,4-dinitro phenyl hydrazone

Special Detection of aldehyde:

ⓐ Silver Mirror Detection (Tollen's reagent) $[Ag(NH_3)_2OH]$: In clean test-tube, put 3 drops from 5% $AgNO_3$ and add 3 drops from 10% NaOH slowly with shake till a precipitate is formed, then add slowly drop by drop with shake 2% NH_4 until the formed precipitate is disappeared :

$$2AgNO_3 + 2NaOH \longrightarrow \underset{\text{Black ppt from silver oxide}}{Ag_2O\downarrow} + 2NaNO_3 + H_2O$$

$$Ag_2O + NH_4OH \longrightarrow \underset{\text{Follen's solution}}{[Ag(NH_3)_2OH]}$$

Put (2 drops) from ald. to the prepared Tollen's solution in the test-tube without shake and carefully to avoid break formed the silver mirror, then put it in water bath and note that the silver mirror will form on the tube walls .

$$2\,Ag(NH_3)_2OH + \underset{\text{aldehyde}}{R-\overset{O}{\overset{\|}{C}}-H} \longrightarrow \underset{\substack{\text{Silver mirror}\\ \text{fromed on the}\\ \text{tube wall}}}{Ag\downarrow} + R-\overset{O}{\overset{\|}{C}}-ONH_4 + 3NH_3 + H_2O$$

$$Ag(NH_3)_2OH + \underset{\text{Ketone}}{R-\overset{O}{\overset{\|}{C}}-R'} \longrightarrow N{\cdot}R$$

This operation repeated with ketones ,we note that silver mirror non-formed ,and the result is negative ,this detection distinguishes between the aldehyde and ketone.

✓

ⓑ chromic acid detection

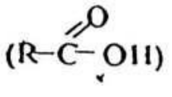
some drops from aldehyde or ketone and some drops from chromic acid the colour reagent convert from brown to green this refer to aldhyde but ketone give anegative.

$$\underset{\text{aldehyde}}{R-\overset{O}{\overset{\|}{C}}-H} + H_2CrO_4 \longrightarrow RCOOH + \underset{\text{green ppt.}}{CrO_3\downarrow}$$

$$\underset{\text{Ketone}}{R-\overset{O}{\overset{\|}{C}}-R'} + H_2CrO_4 \longrightarrow N{\cdot}R$$

IV-Carboxylic Acid

Carboxylic acid are compounds of the general formula:



$$(R-\overset{O}{\overset{\|}{C}}-OH)$$

Take 5 drops of carboxylic compound and add to some drops from sodium bicarbonate ($NaHCO_3$), the acidity of carboxylic acid shown by the evolution of bubbles of CO_2 .

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