ORGANIC CHEMISTRY LABORATORY

UNIVERSITY OF SALAHADDIN – HAWLER

COLLEGE OF EDUCATION

CHEMISTRY DEPARTMENT

Practical Organic Chemistry

FOR SECOND STAGE STUDENTS

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SAFETY AND TECHNIQUE RULES

Safety in the laboratory is extremely important. It is expected that you know laboratory safety rules. It is important that if you feel uncomfortable with your knowledge of these rules that you take the time to learn them. There is *NO* excuse for not following safety rules.

1. Be attentive to instructions and follow them carefully.
2. If you ever have any questions about the procedure, apparatus, or chemicals it is important that you ask the Instructor or Instructional assistant.
3. Do not perform any unauthorized experiments. Anyone found doing so faces permanent expulsion from class.
4. Do not handle chemicals or materials not assigned to you or not called for in the experiment.
5. Learn the location and proper use of the fire extinguisher.Coats, books, etc, should be kept in the good place. Many of the chemicals used in the lab can ruin or stain paper and clothing.
6. Never taste chemicals, nor pipet by mouth. Always use pipet bulbs or wheels.
7. Smell chemicals by fanning a little vapor towards you.
8. Experiments in which dangerous or obnoxious fumes are produced must be done in the fume hood. Be sure to stop these reactions as soon as possible.
9. No eating, drinking or smoking in the lab.
10. Never point test tubes at yourself or others.
11. In the event of any injury, spill or glass breakage, inform the Instructor immediately.
12. Goggles must be worn at all times when in the lab.
13. Chemicals may not be taken out of the lab.
14. Avoid unnecessary contact with ALL chemicals.
15. Do not leave lit burners unattended
16. Every time you use a chemical read its label carefully. If any discrepancies inform the instructor immediately.
17. All containers which contain a chemical or in which a reaction occurs must be labeled.
18. When labeling a storage container include name and/or formula of chemical, any appropriate warnings, concentration, date and your name.
19. NEVER place anything inside a reagent bottle, no spatulas, droppers, nor pipets. Proper technique is to "roll"
20. Containers from side to side to remove solids and to pour liquids into smaller containers (such as a beaker) first.

21. NEVER return unused chemical (liquids or solids) back to the original container offer excess to another student or dispose of it appropriately.
22. Be conservative of reagents; place only the amount you need into a labeled container (such as a beaker). Do not take the reagent bottles to your work area - leave them where everyone can find them.
23. Use tap water to wash glassware - you should rinse with D.W- please be conservative.
24. To dilute acids and bases, add the Acid (or Base) to the Water.
25. Dispose of liquids and solids appropriately, read the board, or your experimental procedure for special instructions, otherwise dispose of liquids and soluble solids down the sink with lots of water, insoluble Is materials (such as paper towels) should be put in the waste basket. KEEP THE SINKS CLEAN
26. It is very important to keep the lab clean. Before you leave each time be sure to:
    a) return equipment to its proper place
    b) clean up your workspace with the sponge
    c) put away your lab ware.

    There is *NO* reason for a messy lab. Everything you need to keep your lab neat and clean is available. Dirty counters, paper left in the sink or troughs, labware left out, messes left under the fume hood, chemical spills left on the balance, are BAD technique and as such will not be tolerated.
27. You may not be in the laboratory at any time other than your scheduled laboratory period unless you have the permission of the instructor in charge as well as your course instructor. Do not v bvsit friends during their lab time and do not invite your friends or family to visit you**.**

EXPERIMENT (1)

MELTING POINT DETERMINATION

Melting point is the temperature at which the first crystal just starts to melt until the temperature at which the last crystal disappears or the temperature at which a solid melts is known as the melting point (MP) of that substance. In practice, a solid usually melts over a range of temperatures rather than at one specific temperature. For this reason it is more useful to speak of a melting point range.

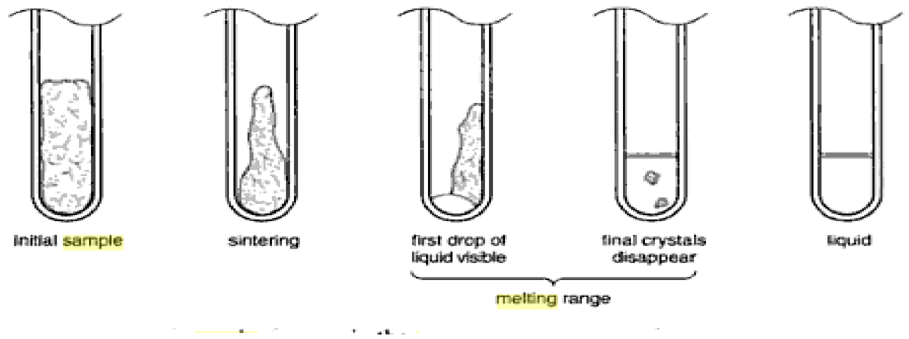
Generally, melting points are taken for two reasons:

The melting point is a physical property of a solid and can be used for:

1- ***Determination of purity***: If the compound melts over a very narrow range, it can usually be assumed that the compound is relatively pure. Conversely, compounds that melt over a wide range are assumed to be relatively impure. Besides melting over a wide range, impure solids also melt at a temperature lower than that for the pure compound. For our purposes a range greater than 2° usually indicates an impure compound. For example, if an unknown solid melts at 102-106° C, the 4° range suggests that the sample is impure.

{(0.5-1) (sharp M.P) very pure}, {(1-2)° pure}, {greater than 2° impure}.

2- ***Identification of unknowns****: The effect of impurities on the MP can actually be used to help identify a compound*. For example if an unknown solid is known to be one of two possible known compounds, both having the same MP, the unknown can be mixed with one of the known compounds and a MP taken of the mixture. If the MP range is lowered and widened, it means that the two are different compounds. If the MP stays the same it means that the two compounds are likely identical. *This technique is known as a mixed melting point determination*.



Typical sample changes in the region of its melting point

The first sign that your sample is about to melt is a contraction in volume of the sample, which may result in it pulling away from the walls of the tube, although no liquid will be visible at this stage. This phenomenon is referred to as sintering and the temp. at which this occurs should be noted. The first droplet of liquid should then be visible with in few degrees of the sintering point and this is considered to be the commencement of melting.

The completion of melting is taken to be the point at which the last crystal disappears. These two readings constitute the M.P.rang

Sample Preparation

Careless preparation of a sample is the leading cause of inaccurate and irreproducible results in melting point determinations. Any substance being loaded into a melting point capillary must be

1. Fully dry
2. Homogeneous
3. In powdered form

To fill a capillary tube with a sample, the open end of the capillary is pressed gently into the substance several times. The powder is then pushed to the bottom of the tube by repeatedly pounding the bottom of the capillary against a hard surface (preferred method). A sample packing wire can be used at the end to further compact the sample and improve the reproducibility of the measurements.

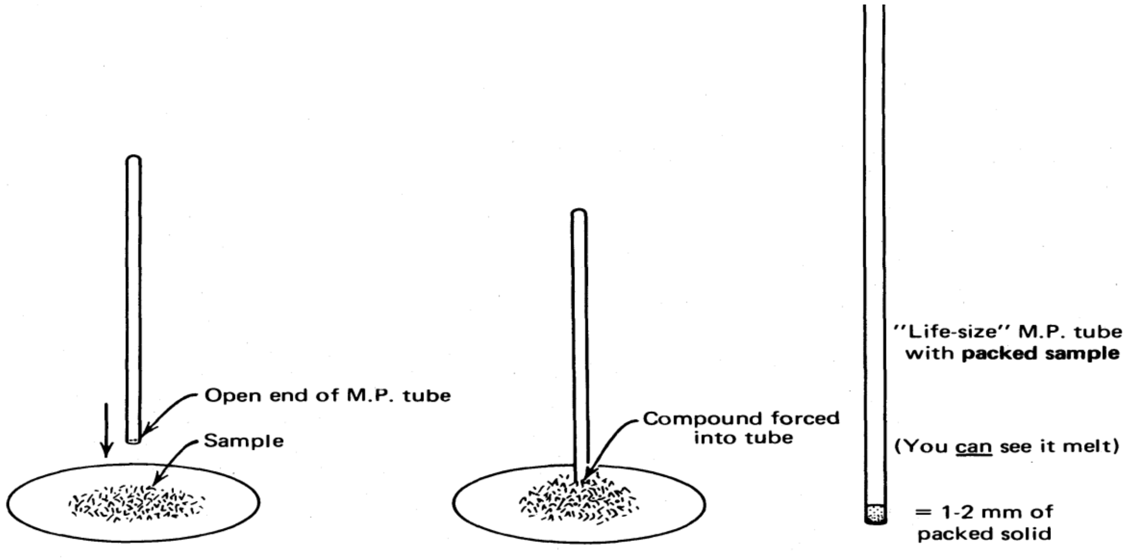


Fig.1 loading a melting point tube

Melting point hints

1- *Use only the smallest amount that you can see melt. Larger sample will heat unevenly.*
2- *Pack down the material as much as you can. Left loose, the stuff will heat unevenly.*
3- *Never remelt any sample. They may undergo nasty chemical changes such as oxidation, rearrangement and decomposition.*
4- *Make up more than one sample. One is easy, two is easier. If something goes wrong with one, you have another. Duplicate, even triplicate runs are common.*

EXPERIMENT (2)

RECRYSTALLISATION OF SOLID SUBSTANCE

Purpose:

a) To purify samples of organic compounds that are solids at room temperature
b) To dissociate the impure sample in the minimum amount of an appropriate hot solvent

The most important method for purifying solids is recrystallization

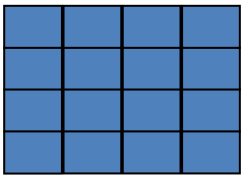
Recrystallization: A purification method in which a desired product is separated from impurities through differential solubility in a hot solvent.

Or Recrystallization is a technique for the purification of chemical compounds in which the compound is dissolved in a hot solvent and slowly cooled to form crystals.

Source of impurities: *(why we do recrystallization?)*

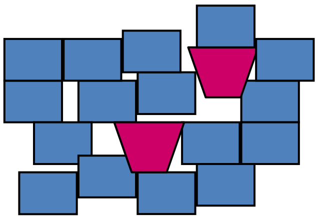
1- The products of chemical reactions can be impure. Purification of your products must be performed to remove by-products and impurities
2- When organic substances are isolated from plants, they will obviously contain impurities.
3- Storage environment.

Recrystallization relies on the different solubility of solutes in a solvent. Compounds which are less soluble will crystallize first.



Pure solid:

Tight crystal lattice



Impurities disrupt

the crystal lattice

Requirements for Recrystallization

- Selection of solvent

- Dissolve the entire compound at the boiling point of the solvent.
- Dissolve very little or none of the compound when the solvent is at room temperature (RT).
- Have different solubilities for the compound and the impurities.

- Filtration of hot solution (gravity filtration).

- Cooling to form crystals again.
- Separation of crystals from the mother liquid (vacuum filtration).
- Drying of crystals.

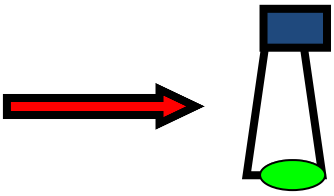
Which Solvent to Choose?

- Compound should dissolve in a reasonable amount of hot solvent, but not in cold solvent.
- The solvent should not react with the compound.
- The solvent should be partially volatile in order to be easily removed from purified crystals (Relatively low boiling point).
- Have a boiling point below the melting point of the compound.
    - Compound dissolves, not melts into the solvent
- The solvent should be nontoxic, low odor and non-flammable.
- The solvent should be available and low cost.

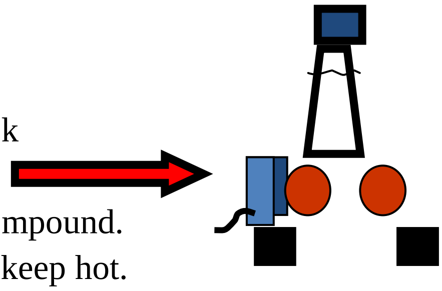
Performing the Recrystallization:

1. Weigh out 1gm of impure compound

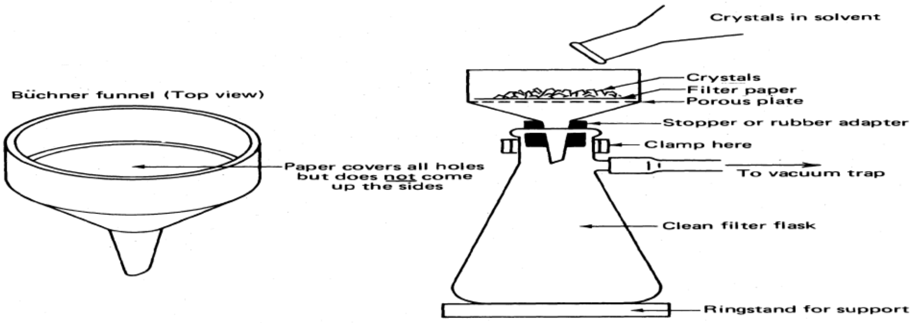
   (benzoic acid) place in 50 ml conical flask



2. Set up hot plate.
    - Place 50 ml of D.W in a 100 ml conical flask
    - Bring to boil



3. Add small amounts of boiling water to the impure compound.
4. Place conical flask + compound back on hot plate to keep hot.
5. Continue to add hot D.W until compound dissolves completely, and then filtrate the hot solution.
6. Remove it from heater, place on bench top to cool to RT.
7. After the conical flask is at RT, place in ice bath for full recrystallization.
8. After about 10 min, remove from ice and vacuum filter.



Q/ Why should the hot filtrate be allowed to cool slowly as the desired product recrystallizes?

EXPERIMENT (3)

SUBLIMATION

Sublimation is the process by which a solid change from the solid to the gaseous state directly without forming a liquid.It is physical property of some substances to pass directly from the solid state to the gaseous state without the appearance of the liquid state. Not all substances possess this characteristic. If one component of a mixture sublimates, this property may be used to separate it from the other components of the mixture. Iodine (I_2), naphthalene ($C_{10}H_8$, mothballs), ammonium chloride (NH_4Cl) and dry ice (solid CO_2) are some substances which sublime; this property is usefully employed as a method of purification.

Sublimation apparatus (finger cold)

Sublimation method use for compound that:

1- Have a relatively high vapor pressure.
2- Have non-volatile impurities.

Sublimation uses:

1- It is a method for purification and separation.
2- It is an excellent method for growing crystals. If the process is slow then the quality of the crystal formation is usually better.

Advantages of sublimation over recrystallization:

1- It usually gives very clean products.
2- Very small amount (minute) can be sublimed.
3- The process is slower and the quality of the crystal formation is better.
4- There is no solubility relation problem.
5- It is also use as separation method.

Disadvantages:

1- Limitation, not suitable for all organic compounds.
2- Sometime the impurity has a vapor pressure similar to that of the product.

Q/ how do you can separate a mixture of NH_4Cl, $NaCl$, SiO_2?

EXPERIMENT (4)

DISTILLATION AND SIMPLE DISTILLATION

DISTILLATION**:** is the purification of a liquid by heating it to its boiling point, causing vaporization, and then condensing the vapors into the liquid state and collecting the liquid. Separation of two or more liquids requires that they have different boiling temperatures. *Distillation is used for many industrial processes, such as production of gasoline and kerosene, distilled water, organic solvents, and many other liquids. There are 4 types of distillation including simple, fractional, steam and vacuum distillations*.

Vapor Pressure and Boiling Point

If a liquid is placed in a closed container, some molecules at the surface of the liquid evaporate into the space above the liquid. If this didn't happen, you wouldn't be able to smell a liquid. At any given temperature a liquid is in equilibrium with its vapor. This equilibrium is described by the vapor pressure of the liquid. ***The vapor pressure is the pressure that the molecules at the surface of the liquid exert against the external pressure, which is usually the atmospheric pressure***. The vapor pressure is a very sensitive function of temperature. It does not increase linearly but in fact increases exponentially with temperature.

When the vapor pressure of the liquid equals the applied pressure, the liquid boils. Thus, ***the boiling point of a liquid is the temperature at which the vapor pressure equals the applied pressure. The normal boiling point of a liquid is the temperature at which the vapor pressure of a liquid equals atmospheric pressure (1 atm).*** The boiling point of a liquid is a measure of its volatility.

Questions:

1- Why should a distilling flask be filled not less than 1/3 filled or more than 2/3 full?
2- What is the purpose of the boiling chips (boiling stones)?

SIMPLE DISTILLATION

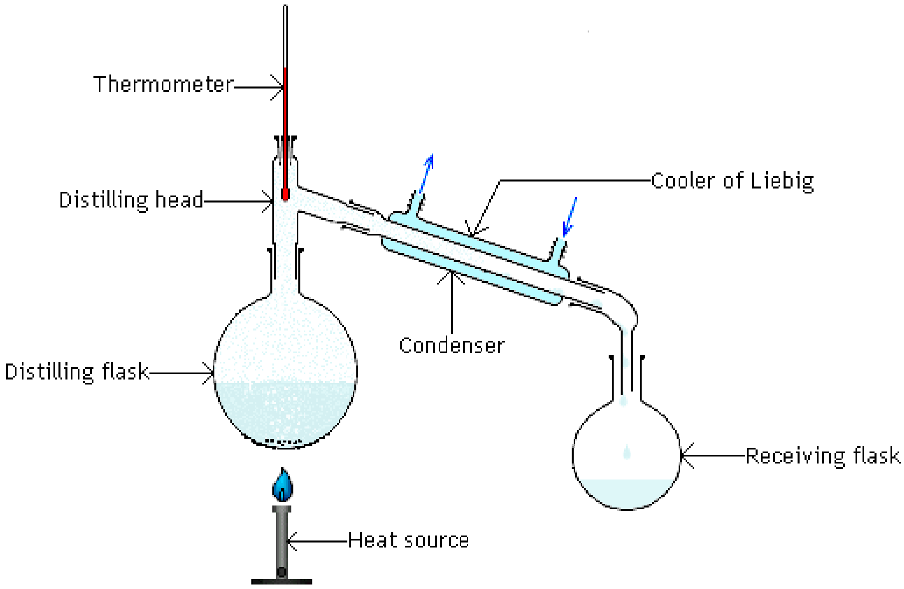
Simple distillation is a physical process used to separate chemicals from a mixture by the difference in how easily they vaporize, is usually used only to separate liquids whose boiling points differ greatly (more than 25°C), or to separate liquids from nonvolatile solids or oils.

All the hot vapors produced are immediately passed into a condenser to cool and condense the vapors back to liquid. Simple distillation involves a single equilibration between the liquid and vapor. This distillation is referred to as involving one theoretical plate. Simple distillation is one of the oldest and still most common methods for both the ***purification*** and the ***identification*** of organic liquids.

Generally Simple Distillation used frequently in the organic chemistry teaching labs, when:

a) To purify a compound by separating it from a non-volatile or less-volatile material.
b) To separate a mixture of two miscible liquids (liquids that mix in all proportions)
c) To determination boiling point of the liquids.

The distillation range of temperature can be an indication of the purity of the liquid. A liquid with a wide boiling or distilling range is impure (similar to the melting point).If the distilling range is narrow and constant during a distillation; it usually means that the liquid is pure.



Simple Distillation apparatus

Procedure:

In the dry round bottom flask add 25 mL of water (containing a purple color). Add one or two tiny boiling chips, attach the boiling flask, and make certain that all connections are tight. Arrange a graduated cylinder to serve as the receiver. Heat the flask gently to boiling, and record the temperature when the first drops of distillate collect in the condenser. As the liquid boils, watch for the condensation line of vapor as it moves up the distilling head. To observe and record an accurate temperature reading, the entire thermometer bulb must be immersed in vapor. Adjust the heater to produce distillate at a rate that is no greater than one drop per 20-30 second.Record the temperature range from the beginning to the end of the distillation; this is the observed boiling point

Questions:

1- Why a distilling flask should be filled not less than 1/3 filled or more than 2/3 full?
2- What is the purpose of the boiling chips (boiling stones)?
3- Why the top of the thermometer bulb must be even with the bottom of the side arm on

EXPERIMENT (5)

FRACTIONAL DISTILLATION

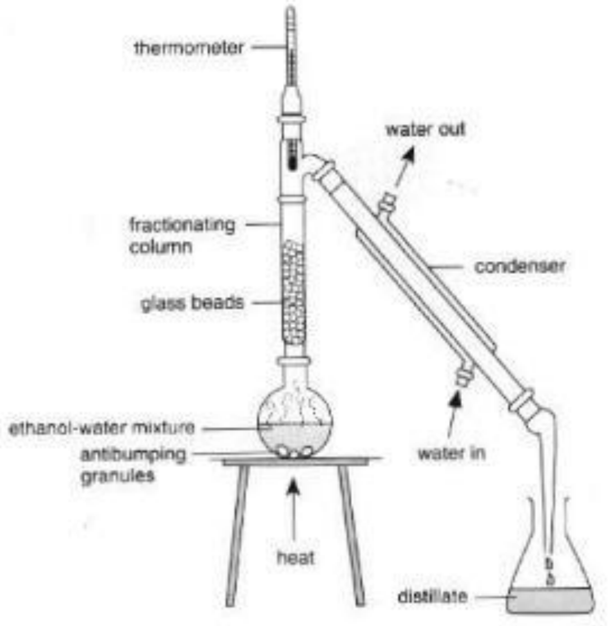
Fractional Distillation- Fractional distillation is a technique used to purify solvents with narrow differences in boiling points less than (25°C), use to separate chemicals, crude oil and natural products. The principle of fractional distillation is based on the establishment of a large number of theoretical vaporization-condensation cycles (theoretical plates), the apparatus of a simple distillation is modified by inserting a fractionating column between the distillation flask and the distillation head, the fractionating column provides a large surface area in which the initial distillate is redistilled and condensed again. This process continues as the vapors rise up the column until the vapors finally make it into the condenser. These vapors and the final distillate will contain a greater percentage of the lower boiling liquid. Continuous repetition of re-distillation process in fractional distillation gives good separation of the volatile liquid components. This number of times that the process of vaporization and condensation occurs depends on the efficiency of the distillation column.

Fractional column:

It is a type of glassware in fractional distillation use to separate a vaporized mixture into its component parts or fractions by a series of condensation-vaporization steps. The longer and more efficient the column, the more times this will happen and the better will be the separation.

Column efficiency (how pure can you get?)

1- A common measure for the efficiency of column is given by its number of theoretical plates.
2- One theoretical plate is equivalent to a simple distillation.
3- The smaller the boiling point difference the greater number of theoretical plates of fractionating column must have to achieve good separation of the mixture.



Fractional distillation apparatus

EXPERIMENT (6)

VACUUM DISTILLATION

Vacuum distillation is a method of distillation whereby the pressure above the liquid mixture to be distilled is reduced to less than its vapor pressure (usually less than atmospheric pressure) causing evaporation of the most volatile liquids (those with the lowest boiling points). This distillation method works on the principle that boiling occurs when the vapor pressure of a liquid exceeds the ambient pressure. *Vacuum distillation is used with or without heating the mixture.*

Laboratory-scale applications

Laboratory-scale vacuum distillation is used when

1- Liquids to be distilled have high atmospheric boiling points (B.p>150^{o}C).
2- They are chemically changed at temperatures near their atmospheric boiling points.
3- Temperature sensitive materials (such as beta carotene) also require vacuum distillation to remove solvents from the mixture without damaging the product. Vacuum distillation is sometimes referred to as low temperature distillation.

Industrial-scale applications

Industrial-scale vacuum distillation has several advantages.

1- Close boiling mixtures may require many equilibrium stages to separate the key components. One tool to reduce the number of stages needed is to utilize vacuum distillation.
2- Vacuum distillation increases the relative volatility of the key components in many applications. The higher the relative volatility, the more separable are the two components.
3- Vacuum distillation is very useful to prevent many chemical reactions which occur at high temp. (Especially above 360^{o}C), during distillation such as polymerization and thermal cracking they are form petroleum coke at temp. above that.

Vacuum distillation can improve a separation by:

- Prevention of product degradation or polymer formation because of reduced pressure leading to lower temperatures.

- Increasing capacity, yield and purity.

Q/what are the advantages of vacuum distillation?

EXPERIMENT (7)

STEAM DISTILLATION

Distillation is a commonly used method to separate liquids. Steam distillation is a process by which volatile organic compounds are separated from non-volatile inorganic salts. Most of the organic compounds break down at high temperatures. When steam is added to the distillation apparatus, the boiling point of the compounds comes down and this allows the organic compound to evaporate at lower temperature.

Steam distillation is used to distill compounds that are *sensitive to heat*. Some organic compounds are temperature sensitive, and *decompose at the temperatures required for simple distillations*; however, by using the properties of *immiscible, or unmixable, liquids, distillation can be performed at much lower temperatures*. Steam distillation is performed by bubbling hot steam through the mixture to be distilled, and collecting the vapor that results. Using steam to heat the mixture ensures that the temperature of the compounds does not exceed 100 degrees. The collected vapor is then condensed, and the resulting fluid consists of a layer of water and a layer of the compound being distilled. These compounds are separate due to the properties of immiscible liquids, and can be physically separated by decanting or the use of a separation funnel.

Raoult’s law

The composition of the mixture being controlled by Raoult’s law.

In an ideal solution the partial pressure (P_A) of component *A* at a given temperature is equal to the vapor pressure $P^o{}_A$ of pure *A* multiplied by the mole fraction of *A* (X_A) in solution.
Consider an ideal solution of *A* and *B*:
$X_A= nA/ (nA+ nB)$,$X_B= nB/ (nA+ nB)$ and$X_A+ X_B= 1$
nA and *nB* represent the number of moles of components A and B.
From Dalton's law, the total vapor pressure of the solution(P_T) is the sum of partial pressures of A and B:
$P_T = P_A+ P_B$ $P_A= X_AP^o{}_A$ *and* $P_B= X_BP^o{}_B$ and
$P_T = X_AP^o{}_A+ X_BP^o{}_B$
The boiling point of the solution is reached when *PT* is equal to the pressure applied to the surface of the solution.

The choice of the steam distillation for the liquid organic compound is generally indicated by the following consideration.

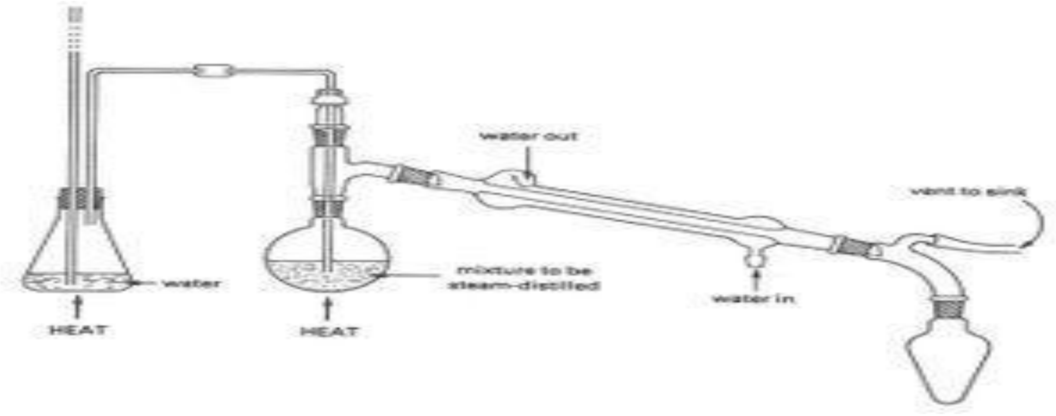
1- Sensitivity of the compound to the action of heat and water.
2- Volatility of the compound.
3- Water solubility of the compound.

Principle

The process is based on the principle that the vapor pressure above the mixture is equal to the sum of individual vapor pressure of the compounds. When vapor pressure is equal to atmospheric pressure, the liquid starts to boil. When steam is passed on to the mixture which contains the mixture of immiscible organic compounds, it gets heated by the steam and itself condenses into water. When vapor pressure above the mixture becomes equal to atmospheric pressure, the resulting mixture of organic compound and water starts to boil until one of the liquids completely distills out. The distillate which is a mixture of water and the organic compound separates into two layers because both the liquids are immiscible with respect to the other. These two layers are separated using a separating funnel.

Applications of Steam Distillation

Steam distillation is used to separate temperature-sensitive organic compounds such as aromatic substances. It can be used to extract oils from natural products, such as eucalyptus oil, citrus oils, or other natural substances derived from organic matter.



Steam Distillation apparatus

EXPERIMENT (8)

SOLVENT EXTRACTION

Extraction is the recovery of a substance from a mixture by bringing it into contact with a solvent, which dissolves the desired material. ***Like recrystallization and distillation, extraction*** *is a separation technique frequently employed in the laboratory to isolate one or more components from a mixture*. ***Unlike recrystallization and distillation***, it does not yield a pure product; thus, the former techniques may be required to purify a product isolated by extraction.

Principle of solvent extraction:

In the technical sense extraction is based on the principle of the ***equilibrium distribution*** *of a substance (solute) between two immiscible phases*, one of which is usually a solvent. The solvent need not be a pure liquid but may be a mixture of several solvents or a solution of some chemical reagent that will react with one or more components of the mixture being extracted to form a new substance soluble in the solution.

The technique of solvent extraction often involves a number of processes.

1- The component mixture is dissolved in a suitable solvent.
2- Solvent that is immiscible with the first solvent is added (e.g., two solvents that are immiscible are diethyl ether and water).
3- The contents are thoroughly mixed (shaking) and the two immiscible solvents allowed separating into layers. The less dense solvent will be the upper layer, while the more dense solvent will be the lower layer. The components of the initial mixture will be distributed amongst the two immiscible solvents as determined by their partition coefficient. Lower layer.
4- Lastly, the two immiscible layers are separated, transferred and the component in that solvent is isolated by solvent evaporation and/or crystallization.

Acid/Base Extraction

There are also three special cases of liquid/liquid extraction (solvent extraction) that are extremely useful for isolating and purifying amines, carboxylic acids and phenols. All three of these functional groups can be interconverted from non-ionic organic-soluble forms to water-soluble ionic forms by changing the pH.

Amines: $RNH_2 + H^+ \rightleftharpoons RNH_3^+$

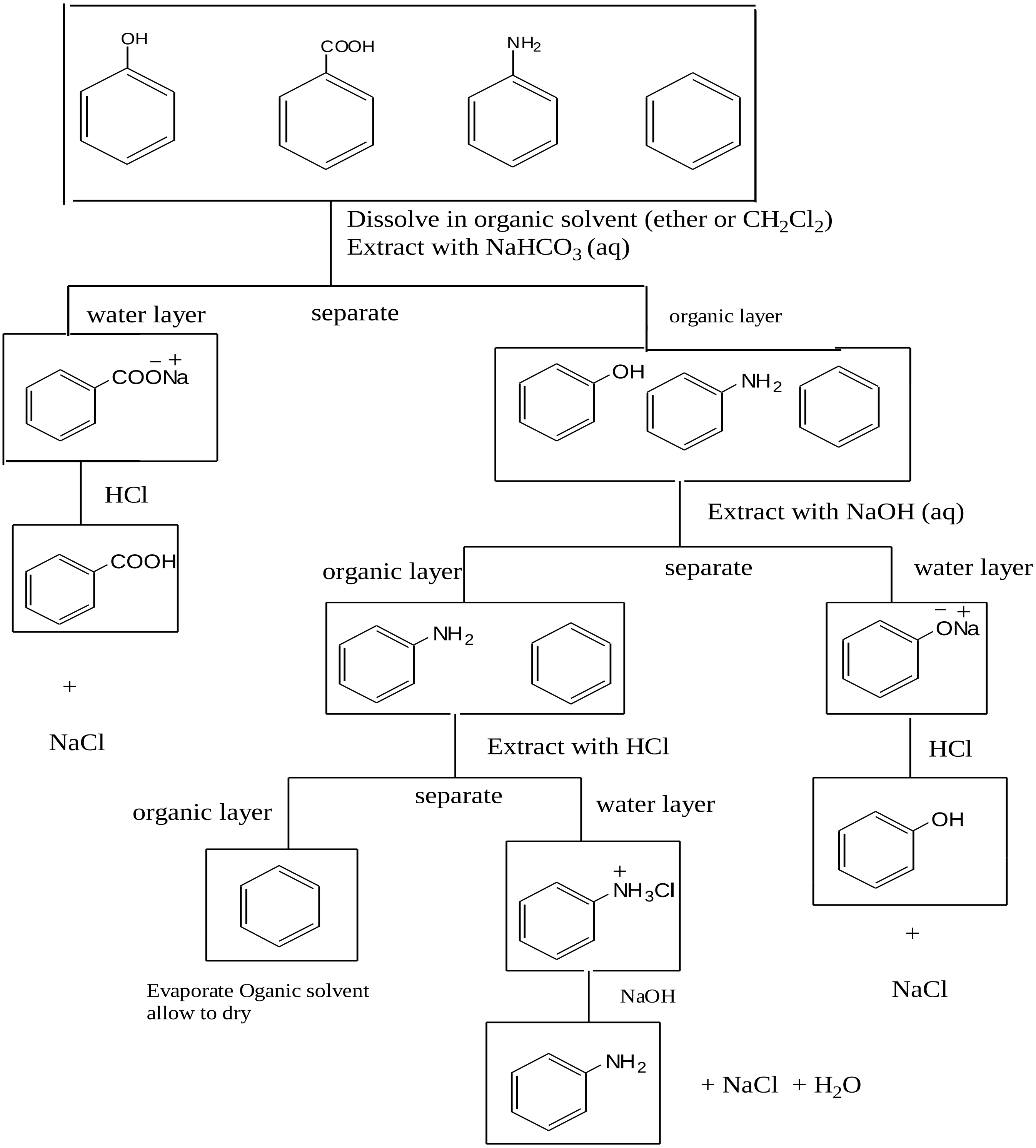
Phenols: $PhOH + OH^- \rightleftharpoons PhO^- + H_2O$

Carboxylic acid: $RCOOH + OH^- \rightleftharpoons RCOO^- + H_2O$

Questions

1- Student during an extraction experiment lost track of which layer is the aqueous layer. How could student determine which layer is which by a simple test?

2- Why must the stopper be removed from the separation funnel before the lower layer is removed?



EXPERIMENT (9)

PREPARATION OF METHANE

Alkanes

Alkanes are saturated hydrocarbons. The main source of alkanes is petroleum products and natural gas. Methane is one of the chief constituents of natural gas. Other alkanes are obtained from fractional distillation of crude petroleum.

Physical properties of alkanes

1. Physical state: Lower molecular weight alkanes are gases. Methane, ethane, propane and butane are gases at ordinary room temperature. Higher alkanes up to those having 17 carbon atoms are liquids; higher alkanes are solids at room temperature.
2. Melting and boiling points: Homologous alkanes show increase in melting and boiling points. Similar to the behavior of elements in the same group in a periodic table
3. Solubility: Alkanes, like all other organic chemicals are insoluble in water. They are however soluble in organic liquids. Alkanes are non-polar and are hence soluble in other non-polar liquids and not in water, as water is a polar molecule.

Chemical properties of alkanes

1. **Combustion**: Alkanes are inflammable and are easy to catch fire. Complete combustion of an alkane leads to carbon dioxide and water. During combustion, the supply of oxygen has to be sufficient. Insufficient oxygen leads to carbon monoxide reaction and the heat generated is less than when sufficient oxygen is available. The reactions are given below

$$CH_4 + 2O_2 \xrightarrow[\text{combustion}]{\text{Complete}} CO_2 + 2H_2O + \text{Heat}$$

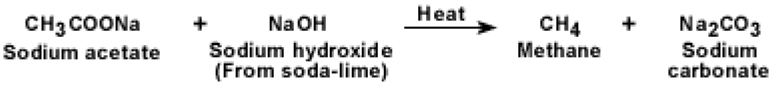
$$2CH_4 + 3O_2 \xrightarrow[\text{combustion}]{\text{Incomplete}} 2CO + 4H_2O + \text{Heat}$$

2. **Substitution reaction:** In alkanes, substitution reactions take place easily by replacement of hydrogen atoms with more reactive atoms. Chlorine is one such example.

$$CH_4 + Cl_2 \xrightarrow{\text{Sunlight}} CH_3Cl + HCl$$

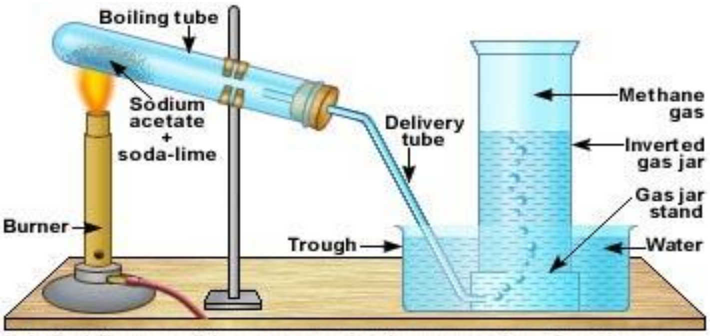
Laboratory preparation of methane gas

In the lab methane is prepared using the following chemical reaction.



$$CH_3COONa + NaOH \xrightarrow{\text{Heat}} CH_4 + Na_2CO_3$$

Sodium acetate is the sodium salt of acetic acid. Sodium hydroxide (NaOH) is obtained from soda lime which is a combination of NaOH +CaO (in the ratio 1:3). Only the NaOH component of the soda lime reacts in the reaction



Labelled diagram of the apparatus for the preparation of methane gas.

A mixture of sodium acetate and soda lime in the ratio 1:3 by weight are taken in a glass tube and heated. Methane gas is evolved which is collected by downward displacement of water. The downward displacement method makes other soluble gases or salts evaporating from the tube to be absorbed. Also it must be remembered that methane is insoluble in water, hence the downward displacement technique can be usefully employed.

Physical properties of methane

Methane (CH_4) is an odourless, colourless, tasteless gas. It is lighter than air. It is a non-polar molecule and is insoluble in water. It dissolves in non-polar solvents like alcohol, carbon tetrachloride, etc.

Uses of methane

1- Because of its excellent burning, methane is used as a cooking gas.
2- Methane is used to produce carbon dioxide gas.
3- Methane is used to produce carbon black used in rubber industries .
4- Methane is used as a starting material for other organic compounds like methyl chloride, methylene dichloride, chloroform, etc.

EXPERIMENT (10)

PREPARATION OF ETHENE

Alkenes

Alkenes are hydrocarbons that have one double bond. They have, as we have seen earlier, sigma and pi bonds. The pi bonds are unsaturated and hence alkenes are known as unsaturated hydrocarbons. Alkenes are more reactive than their alkane counterparts due to the presence of unsaturated pi bonds. Ethene is the first member of the homologous series of alkenes ($CH_2 = CH_2$). Ethene is also known commonly as ethylene. Its IUPAC name is ethene.

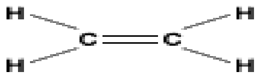
Ethene

Ethene is an odourless, colourless and tasteless gas at ordinary room temperatures. It is insoluble in water. The molecular, electronic and structural formula of ethene is shown below.

C_2H_4

Molecular formula of ethene

Electronic formula of ethene



Structural formula of ethene

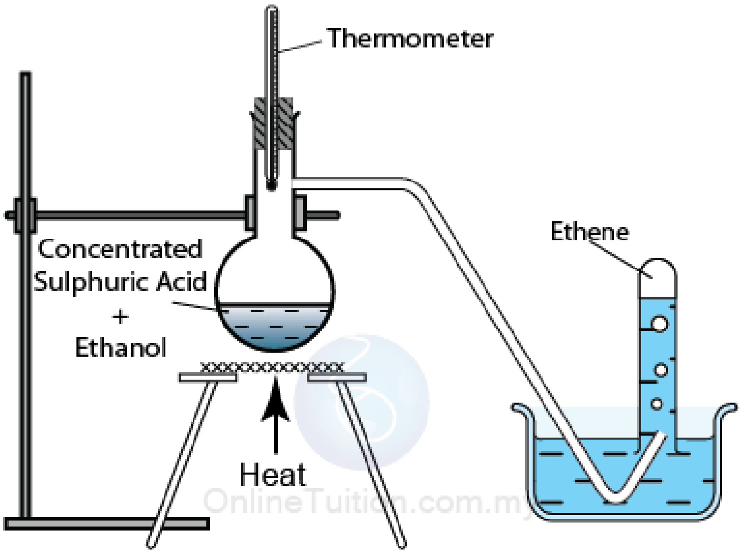
Ethene is found in coal gas and in natural gas to some extent. In laboratory, ethene can be prepared by cracking of large alkane molecules. Cracking is a process whereby large organic molecules are heated and broken up into smaller organic molecules.

Laboratory preparation of ethene gas.

To obtain pure ethene gas, another method is followed. This is from a chemical reaction with ethanol and concentrated sulphuric acid.

$$CH_3{-}CH_2OH \xrightarrow[(-H_2O)]{\text{Conc. } H_2SO_4\ ;\ 160^{\circ}C} CH_2{=}CH_2$$

Ethanol or Ethyl alcohol — **Ethene or Ethylene**



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Procedure:

Place 20 ml. (16 g.) of ethanol in a side armed conical flask, and add slowly, with cooling and shaking, 40 ml1 (74 g.) of concentrated sulphuric acid. Connect up the apparatus and heat it over the sand-bath.
Carry out the following tests with the jars of ethylene.

1- *Odour*. Smell the contents of one of the jars.
2- *Bromine***.**

$$H_2C{=}CH_2 + Br_2 \quad \rightarrow \quad BrCH_2\text{-}CH_2Br$$

Ethene red color dibromoethane (colourless)

The decolourisation of red color of bromine is a test for an unsaturated organic compound.

3- *Alkaline Potassium Permanganate***.**

The alkenes are readily oxidised by potassium permanganate to form glycols. For example, ethene is oxidized to ethylene glycol.

$3\ H_2C{=}CH_2 + 2\ KMnO_4 + 4\ H_2O \implies 2MnO_2 + 2KOH + 3CH_2OHCH_2OH$

Purple color brown color Ethylene Glycol

During the oxidation of alkenes, the purple colour of the permanganate solution disappears and the reaction constitutes a test, known as **Baeyer's Test**, to detect unsaturation in any compound it is a second test for an unsaturated organic compound.

Physical properties of alkenes

The low molecular weighted alkenes such as ethene, propene and butene are gases at room temperature. Alkenes with five to 15 carbon atoms are liquid at room temperature. Higher molecular weighted alkenes are solids at room temperature. Alkenes are insoluble in water but are soluble in organic liquids.

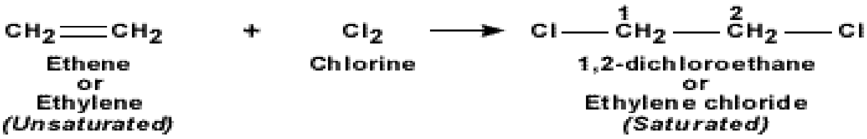
Chemical properties of ethene:

1. Combustion: ethene burns in air with a sooty flame. It forms carbon dioxide and water and gives out heat.

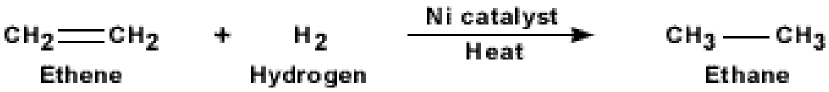
$$H_2C = CH_2 + 3O_2 \longrightarrow 2CO_2 + 2H_2O + \text{heat}$$

The sooty flame is due to higher amount of carbon in ethene than in methane. All the carbon atoms cannot get oxidized while burning, this makes the flame sooty.

2. Reactivity (addition reactions): Alkenes are more reactive than the alkanes due to the presence of unsaturated bonds. The pi bond is not localized and hence can be broken easily in a reaction. Such a reaction is called addition reaction. In an addition reaction, the pi bond converts into a sigma bond and the alkene will become an alkane. For example if ethene is reacted with chlorine, it becomes 1, 2-dichloroethane.

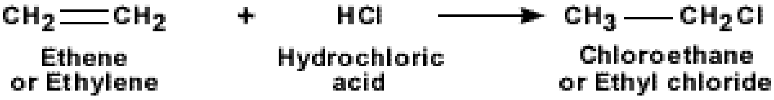


When hydrogen is added to ethene, and heated in the presence of nickel, it becomes ethane.



This is known as the process of hydrogenation. The addition of hydrogen to a double or triple bonded hydrocarbon leads to saturation of the bonds. Such processes are used for hydrogenation of oils.

When hydrochloric acid is added to ethene, it becomes chloroethane. The reaction is shown below.



Similar test with bromine is also used extensively. Bromine water decolorizes on reaction with ethene. This is a prominent test for testing unsaturated nature of hydrocarbons.

with ethene.

Uses of ethene

- Ethene is used for manufacturing organic compounds such as ethyl alcohol and ethylene glycol. Ethylene glycol is used for making artificial fibbers like polyesters.
- Ethene is used for manufacture of plastics. These plastics are made from polymerization of ethene into polythene. Polythenes are used for making bags, electrical insulation, etc.
- Ethene is used artificial ripening of fruits such as mangoes, bananas, etc.

EXPERIMENT (11)

PREPARATION OF ETHYNE

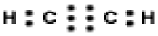
Alkynes

Alkynes are hydrocarbons that have triple bonded carbon atoms. The carbon atoms are bonded together by one sigma bond and two pi bonds. The pi bonds are not localized and hence these hydrocarbons are unsaturated. Alkynes are more reactive than their alkene and alkane counterparts. Ethyne is ($CH \equiv CH$) is the first member of the homologous series of alkynes. Its molecular formula is C_2H_2. The other members are propyneC_3H_4, butyneC_4H_6, pentyneC_5H_8, etc. Ethyne is known commonly as acetylene. Its IUPAC name is ethyne.

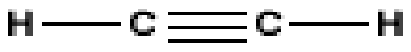
Ethyne

Ethyne is a colourless and tasteless gas at ordinary room temperatures. It smells slightly like ether. It is insoluble in water. The molecular, electronic and structural formula of ethyne is shown below. Ethyne or acetylene gas is a linear molecule.

Molecular formula of ethyne



Electronic formula of ethyne



Structural formula of ethyne

Ethyne is found in coal gas to some extent. In the laboratory, ethyne can be prepared by cracking of large alkane molecules.

Physical properties of alkynes.

The low molecular weighted alkynes such as ethyne, propyne and butyne are gases at room temperature. Alkynes with five to 13 carbon atoms are liquid at room temperature. Higher molecular weighted alkynes are solids at room temperature. Alkynes are insoluble in water but are soluble in organic liquids. Gaseous alkynes can produce a feeling of anesthesia when inhaled.

Chemical properties of ethyne

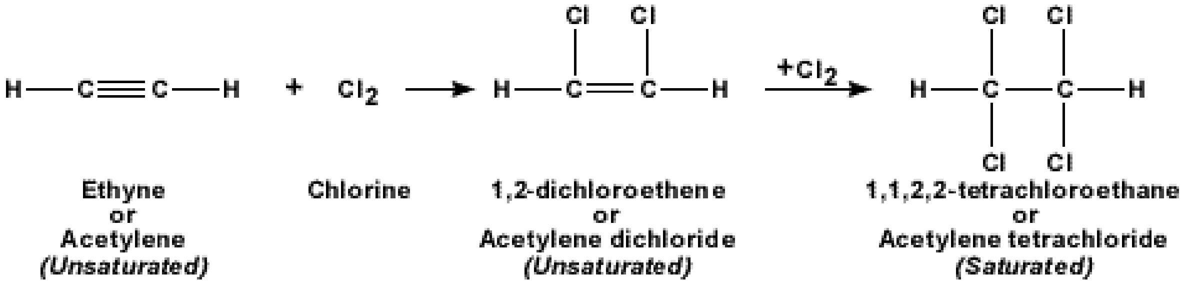
1. Combustion: ethyne burns in air with a sooty flame. It forms carbon dioxide and water and gives out heat.

$$2HC \equiv CH + 5O_2 \longrightarrow 4CO_2 + 2H_2O + \text{heat}$$

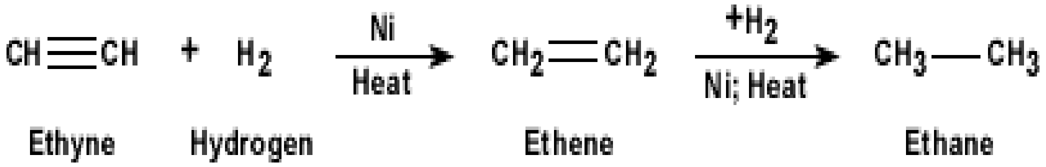
The sooty flame is due to higher amount of carbon in ethyne than in methane. All the carbon atoms cannot get oxidized while burning this makes the flame sooty. But if ethyne is burnt with a proper control, for example, if the gas is made to pass through a small nozzle, then it gets ample air mixture to burn completely. This type of complete combustion is used for acetylene lamps in industries. Acetylene lamps produce very luminous non-sooty flame.

Ethyne combined well with oxygen can burn to give a flame whose temperature is 3000°C. This oxy-acetylene flame is used for welding metals, where very high temperatures are required.

2. Reactivity: Alkynes are more reactive than the alkanes or alkenes due to the presence of unsaturated bonds. The pi bond is not localized and hence can be broken easily in a reaction. Such a reaction is called addition reaction. For example if ethyne is reacted with chlorine, it becomes 1,1,2,2 tetra-chloro-ethane.



When hydrogen is added to ethyne, and heated in the presence of nickel, it becomes ethene and then proceeds to become ethane. The bonds become saturated.



This is known as the process of hydrogenation. The addition of hydrogen to a double or triple bonded hydrocarbon leads to saturation of the bonds.

When hydrochloric acid is added to ethyne, it becomes first chloro-ethene and then 1,1, dichloro-ethane. The reaction is shown below.

$$CH \equiv CH + HCl \longrightarrow CH_2 = CHCl \xrightarrow{+HCl} \overset{1}{C}H_3 - \overset{2}{C}HCl_2$$

Ethyne or Acetylene; Hydrochloric acid; Chloroethene or Vinyl chloride; 1,1-dichloroethane or Ethylidene chloride

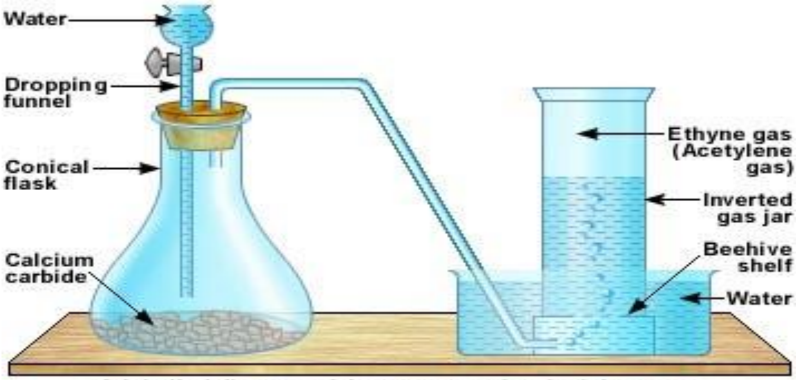
Laboratory preparation of ethyne gas.

In the lab ethyne is prepared by the action of water on calcium carbide. The chemical equation is:

$$CaC_2 + 2H_2O \longrightarrow C_2H_2 + Ca(OH)_2$$

Calcium carbide; Water; Ethyne (or Acetylene); Calcium hydroxide

The apparatus used for producing the ethyne gas is shown below.



A labelled diagram of the apparatus for the laboratory preparation of ethyne or acetylene.

Procedure:

Water is slowly dropped on small pieces of calcium carbide kept in a conical flask. Calcium carbide reacts with water to give off ethyne gas (or acetylene gas). The gas is collected by downward displacement of water as it is insoluble in water.

Tests for ethyne gas

Terminal alkynes (i.e 1-alkynes) undergo a reaction in the presence of silver ion, whereas other alkynes and alkenes do not. Terminal alkynes form salts (acetylides) due to their weakly acidic hydrogen.

$$HC \equiv CH \xrightarrow[H_2O]{Ag(NH_3)_2OH} CH \equiv CAg \downarrow$$

Uses of ethyne

- Ethyne burns in oxygen to give a very luminous light. It is useful in acetylene lamps to generate light.
- Ethyne is used for oxy-acetylene flame used for industrial welding.
- Ethyne is used for manufacture of synthetic plastics, synthetic rubbers, and synthetic fibers.
- Ethyne is also used making many industrially useful organic compounds like acetaldehyde, acetic acid, etc

EXPERIMENT (12)

DETECTION OF ELEMENTS

The important test for identification of organic unknown is the detection of elements. The elements is usually detected are N, S and the halogens (F,Cl,Br,I) whereas C and H are always assumed to be present . For the detection of elements the organic substance is first decomposed by fusion with sodium metal to prepare an extract, called sodium fusion extract.

It is a general test for the detection of halogens, nitrogen and sulfur in an organic compound. These elements are covalently bonded to the organic compounds. In order to detect them, these have to be converted into their ionic forms. This is done by fusing the organic compound with sodium metal. The ionic compounds formed during the fusion are extracted in aqueous solution and can be detected by simple chemical tests.

Procedure:

Freshly cut a very small piece of sodium metal and dry in the folds of a filter paper (sodium is dangerous, therefore , handle it carefully).Use a sharp knife to cut sodium. Never throw scraps of sodium in water. Place the sodium piece in an ignition tube held with a pair of tongs. Heat the lower part of the tube on a flame until sodium melts. Remove the tube from the flame and rapidly add a small amount (0.2 g of the solid or 4 drops of the liquid) of the sample directly over the melted sodium. Again heat the tube to redness, a brisk reaction is observed. Remove the tube from the flame, add another small portion of the unknown sample and heat the tube again till it is red hot. Then immediately immerse the tube in 15 ml of D.W. taken in a china dish, and crush into small pieces with a glass rod. This will hydrolyze sodium and dissolve the ions in water. Boil the mixture for 5 minutes and filter hot to remove the glass splinters.The alkaline filtrate so obtained is usually called sodium fusion extract. This solution is used in subsequent tests for elemental analysis.

$$C, N \xrightarrow[\text{(ii) } H_2O]{\text{(I) Na}} Na^+CN^-$$

$$S \longrightarrow Na_2^+ S^{2-}$$

$$X \longrightarrow Na^+ X^-$$

$$X = Cl, Br, I$$

During this process sodium metal combine with the elements present in the sample and converts into water soluble salts as shown in the above equations.

a) Tests for Nitrogen (Lassaign’s test)

Take 1ml of sodium fusion extract in a test tube and add 2 drops of freshly prepared saturated ferrous sulfate solution. A green ppt. should be obtained. In case no such ppt. is obtained, add a few drops of sodium hydroxide solution. At this stage a green ppt. should appear. The green ppt. is due to the formation of $Fe(OH)_2$ and not due to the presence of nitrogen. Ferrous hydroxide reacts with sodium cyanide to form sodium ferrocyanid. Boil the mixture for 10 sec. and acidify with dil. sulfuric acid, while shaking till a clear solution is obtained. A Prussian blue color indicates the presence of nitrogen. This is called Lassaign’s test.

$$Fe\ SO_4 + 2\ NaOH \longrightarrow Fe(OH)_2 + Na_2SO_4$$

$$Fe(OH)_2 + 6NaCN \longrightarrow Na4[Fe(CN)_6] + 2NaOH$$

$$3Na_4[Fe(CN)_6] + 2\ Fe2(SO4)_3 \longrightarrow Fe_4[Fe(CN)_6]_3 + 6Na_2SO_4$$

On boiling the alkaline solution some ferric ions are produced by the oxidation of the ions by air. Both ferrous and ferric hydroxides dissolve on adding dil.sufuric acid. The ferrocynide reacts with ferric ions to produce the Prussian blue color of ferri-ferrocyanide.

The alkaline solution should not be acidified by hydrochloric acid because the yellow color due the ferric chloride formed causes Prussian blue to appear greenish. Ferric chloride, as is usually recommended, should not be added for the same reason.

b) Tests for Sulfur

1- Lead sulphide test:

The presence of sulfide ion and hence of sulfur in the sodium extract is easily detected since many metal ions (Pb, Ag, etc.) form insoluble sulfides. In a test tube acidify 1ml of sodium extract with dilute acetic acid. In acid any sulfide ion present is converted to hydrogen sulfide gas. Add 1-2 drops of lead acetate solution (preferably saturated solution). The appearance of black ppt. due to the formation of lead sulfide indicates sulfur.

$$Na_2S + 2CH_3COOH \longrightarrow 2CH_3COONa + H_2S$$

$$(CH_3COO)_2Pb + H_2S \longrightarrow PbS + 2CH_3COOH$$

Sometimes a brownish ppt. is formed which indicates sulfur containing impurities in the sample.

2- Sodium nitroprusside test: Add 1-2 drops of freshly prepared solution of sodium nitroprusside to 0.5 ml of the sodium fusion extract in a test tube. A deep red or violet color confirms sulfur

$$Na_2S + Na_2[Fe(CN)_5NO] \longrightarrow Na_4[Fe(CN)_5NOS]$$

d) Tests for Halogens

Silver nitrate test

1-In the presence of nitrogen or sulphur or both:

If the sample contains nitrogen or sulfur or both these elements they should be removed in the form of gaseous compound because cyanide and sulphide ions both interfere with this test for halide by forming silver cyanide and silver sulphide precipitates respectively with silver nitrate, therefore the interfering ions must be removed by acidification with conc. nitric acid and boiling.

$$NaCN + HNO_3 \longrightarrow HCN + NaNO_3$$

$$Na_2S + 2HNO_3 \longrightarrow H_2S + NaNO_3$$

Acidify 1ml of sodium fusion extract with 1 ml conc. Nitric acid and boil. Cool and add several drops (0.5 ml) of silver nitrate solution:

* White precipitate formed in case of chlorine (Cl).

* Pale yellow precipitate formed in case of bromine (Br).

* Yellow precipitate formed in case of iodine (I).

2-In the absence of nitrogen or sulphur:

In a test tube add 1ml of filtrare and about 1-2 ml dil. HNO_3 followed by the addition of about 1 ml of $AgNO_3$ solution and observe the results and described the above.

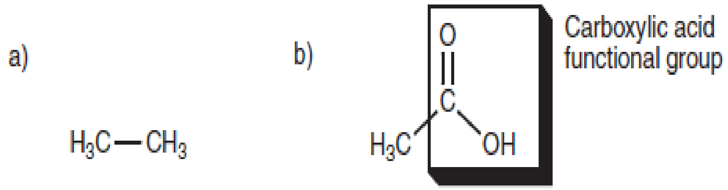
$$NaX + AgNO_3 + HNO_3 \longrightarrow AgX + NaNO_3$$

The above test shows the presence of halogens in the sample. Since all the halogens precipitate in this test as **AgX**. Fluorine is not detected in this test since silver fluoride is soluble in water.

FUNCTIONAL GROUPS

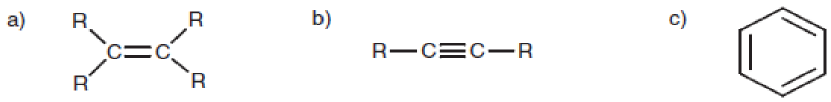
Learning to Recognize Functional Groups of Organic Compounds

A ***functional group*** is a portion of an organic molecule which consists of atoms other than carbon and hydrogen, or which contains bonds other than C–C and C–H bonds responsible for the chemical properties of a compound. For example, ethane is an alkane and has no functional group. All the atoms are carbon and hydrogen and all the bonds are C–C and C–H. Ethanoic acid on the other hand, has a portion of the molecule (boxed portion) which contains atoms other than carbon and hydrogen, and bonds other than C—H and C—C. This portion of the molecule is called a functional group – in this case a carboxylic acid



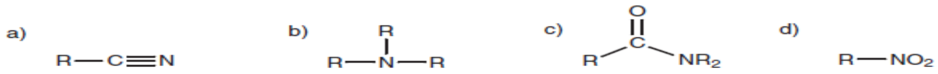
The following are some of the more common functional groups in organic functional groups chemistry.

1- functional groups which contain carbon and hydrogen only



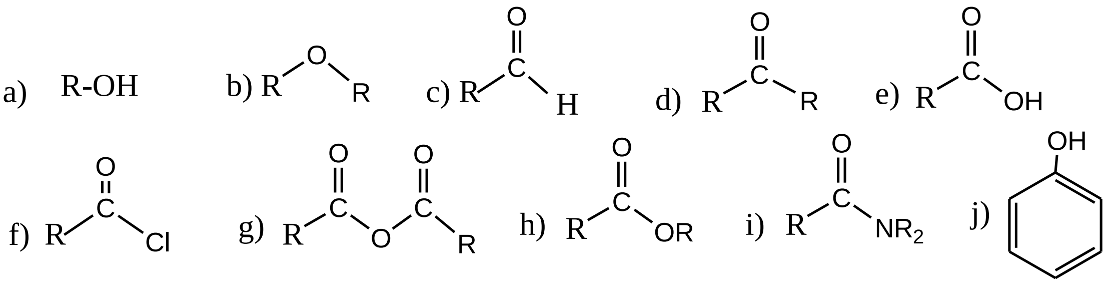
(a) Alkene; (b) alkyne; (c) aromatic

2- functional groups which contain nitrogen



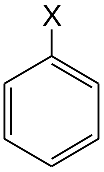
(a) Nitrile; (b) amine; (c) amide; (d) nitro.

3- functional groups involving C-O and C=O



a) acohol b) ether c) Aldehyde ; (d) ketone; (e) carboxylic acid; (f) carboxylic acid chloride; (g) carboxylic acid anhydride; (h) ester; (i) amide; (j) phenol

4- functional groups which contain a halogen atom

a) 

b) R-X

(a) Aryl halide (X_F, Cl, Br, I); (b) alkyl halide or halogenoalkane (X=F, Cl, Br, I)

6- functional groups which contain sulfur

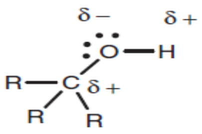
a) R—SH b) R—S—R

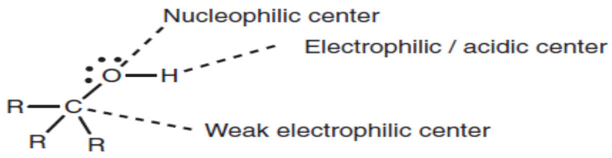
(a) Thiol (b) thioether

EXPERIMENT (13)

DETECTION OF ALCOHOLS

The alcohol functional group (R_3C–OH) has the same geometry as water, with a C–O–H bond angle of approximately 109A^o. Both the carbon and the oxygen are sp^3hybridized. The presence of the O–H group means that intermolecular hydrogen bonding is possible which accounts for the higher boiling points of alcohols compared with alkanes of similar molecular weight. Hydrogen bonding also means that alcohols are more soluble in protic solvents than alkanes of similar molecular weight. In fact, the smaller alcohols (methanol, ethanol, propanol, and *tert*-butanol) are completely miscible in water. With larger alcohols, the hydrophobic character of the bigger alkyl chain takes precedence over the polar alcohol group and so larger alcohols are insoluble in water. The O–H and C–O bonds are both polarized due to the electronegative oxygen, such that oxygen is slightly negative and the carbon and hydrogen atoms are slightly positive. This means that the oxygen serves as a nucleophilic center while the hydrogen and the carbon atoms serve as weak electrophilic center.





1-Effervescence with sodium

In a dry test tube take 2ml of a given compound add 1g of anhydrous Na_2SO_4 (to absorb water already present) and filter, to the filtrate add a small piece of sodium metal. There is effervescence with evolution of hydrogen gas if the substance is an alcohol

$$2ROH + 2Na \longrightarrow 2RONa + H_2$$

2- Ceric ammonium nitrate test

Dissolve 0.5ml of the unknown compound in 1ml of water(or dioxane for water insoluble compounds) and add 1ml of ceric ammonium nitrate solution. Shake the mixture. A red color is obtained if alcohols are present whereas phenols give a green-brown color.

$$\underset{\text{Yellow}}{ROH + (NH_4)_2Ce(NO_3)_6} \longrightarrow \underset{\text{red complex}}{[(NH_4)_2Ce(NO_3)_5(OR)] + HNO_3}$$

3-Distinction between primary, secondary, and tertiary alcohols

Once it has been established that an alcoholic group is present, the next logical step is to distinguish between primary, secondary and tertiary alcohols. To achieve this, the unknown is treated with a reagent and the distinction is then made either on the timing of the reaction between the reagent and the compound or on the separation of the different products. The Lucas test utilizes the former concept. This test may be used only with water soluble alcohols.

Add 3-4 drops of alcohols to 2ml of Lucas reagent (anhydride zinc chloride + conc.HCl) in a test tube, shake the mixture and then allow to stand at room temperature. Immediate separation of two phases due to the formation of an insoluble chloride indicates tertiary alcohol. A cloudy solution is produced in 5-10 minutes in the case of secondary alcohol, while the solution remains clear for primary alcohols (may be cloudy after 30 min.).

Immediate separation of two phases

A cloudy solution in 5-10 minutes

$$R-\overset{H_2}{C}-OH + ZnCl_2 \xrightarrow{HCl} R-\overset{H_2}{C}-Cl + H_2O$$

A cloudy solution after 30 minutes

A positive test depends on the fact that alcohol is soluble in the reagent while alkyl chloride is not. This test fails if zinc chloride is not anhydrous or if the reagent had been setting on the shelf for a long time. In case of doubt whether the alcohol is tertiary or secondary, conc. Hydrochloric acid may be employed. To 1ml of alcohol in a test tube add 5ml of conc. hydrochloric acid and shake. A layer of alkyl chloride separates immediately in the case of tertiary alcohol but secondary alcohols react slowly and the solution remains clear (or it may become turbid after sometime).

4) Chromic acid test

A rather rapid test for distinguish a tertiary from secondary and primary alcohols involves the oxidation with chromic anhydride. Dissolve 1g of chromic anhydride in 10 ml of conc. H_2SO_4 or chromic acid and pour the solution slowly with constant stirring into 30ml of D.W. Cool the resultant deep orange solution. This is the oxidizing reagent. Dissolve 1drop (10 mg) of the unknown alcohol in 1ml of pure acetone.

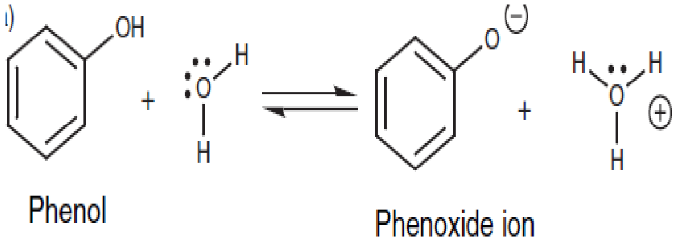
Add 1 drop of the above reagent while shaking, the orange color disappears. Primary and secondary alcohols react to give a ppt. that causes the solution to become opaque with a greenish or greenish blue tint. Tertiary alcohols do not react and the test solution remains orange. Any of these changes taking place after 2 in may disregarded. For the success of this test the sample should not contain an aldehyde function.

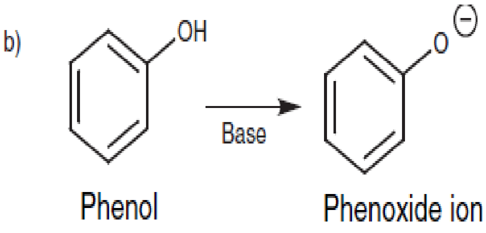
$$3RCH_2OH + 4\ CrO_3 + 6H_2SO_4 \longrightarrow 3RCOOH + 2Cr_2(SO_4)_3 + 9H_2O$$

EXPERIMENT (14)

DETECTION OF PHENOLS

Phenols are compounds which have an OH group directly attached to an aromatic ring. Therefore, the oxygen is sp3 hybridized and the aryl carbon is sp2 hybridized. Although phenols share some characteristics with alcohols, they have distinct properties and reactions which set them apart from that functional group. Phenols can take part in intermolecular hydrogen bonding, which means that they have a moderate water solubility and have higher boiling points than aromatic compounds lacking the phenolic group. Phenols are weakly acidic, and in aqueous solution an equilibrium exists between the phenol and the phenoxide ion (a). On treatment with a base, the phenol is fully converted to the phenoxide ion (b). The phenoxide ion is stabilized by resonance and delocalization of the negative charge into the ring, which means that phenoxide ions are weaker bases than alkoxide ions. This in turn means that phenols are more acidic than alcohols, but less acidic than carboxylic acids.





The pK_a values of most phenols are in the order of 11, compared to 18 for alcohols and 4.74 for acetic acid. This means that phenols can be ionized with weaker bases than those required to ionize alcohols, but require stronger bases than those required to ionize carboxylic acids. For example, phenols are ionized by sodium hydroxide but not by the weaker base sodium hydrogen carbonate. Alcohols being less acidic are not ionized by either base whereas carboxylic acids are ionized by both sodium hydroxide and sodium hydrogen carbonate solutions. These acid–base reactions permit a simple way of distinguishing between most carboxylic acids, phenols, and alcohols. Since the salts formed from the acid–base reaction are water soluble, compounds containing these functional groups can be distinguished by testing their solubilities in sodium hydrogen carbonate and sodium hydroxide solutions.

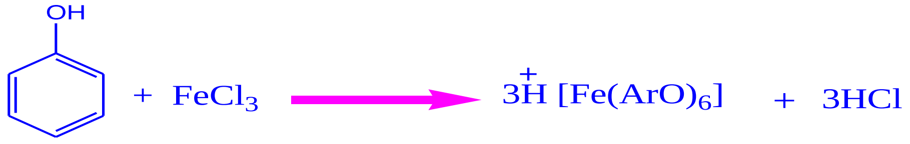
1-Ferric chloride test

To 1ml of a dilute solution (50mg in 1ml of water or aqueous methanol or ethanol) of phenol, add 1-2 drops(only)of 5%neutral ferric chloride solution. A colored solution of a complex is produced.

Observation of colors in $FeCl_3$ addition to phenols

Color observed	Compound class
Blue or bluish violet	Resorcinol, Cresols, Phloroglucinol, Salicylic acid
Green(darkens rapidly)	Catechol
Violet(purple)	Phenol, *p*-bromophenol, *p*-chlorophenol
Reddish brown	Pyrogallol
Often a white ppt.	α- Naphthol
Green	β- Naphthol

The color produced may not be permanent; therefore, observation should be made at the **time of addition.**

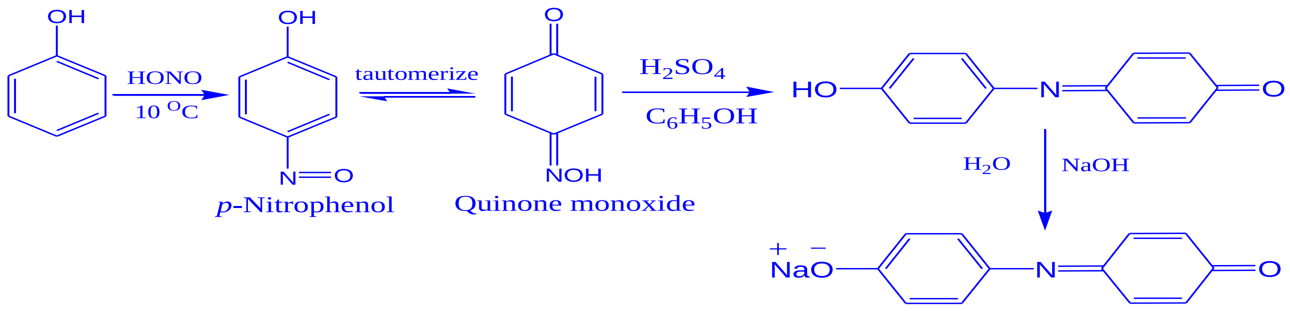


The reaction takes place in polar solvents, therefore, a few drops of pyridine are needed if it is carried out in a non-polar solvent, (ether, benzene, etc.).

Addition of acids destroys the color in this test; p-hydroxybenzoic acid does not give color for this reason. Slicylic acid, on the other hand gives a blue color because it forms a strong complex with ferric chloride

2- Liebermann test (×)

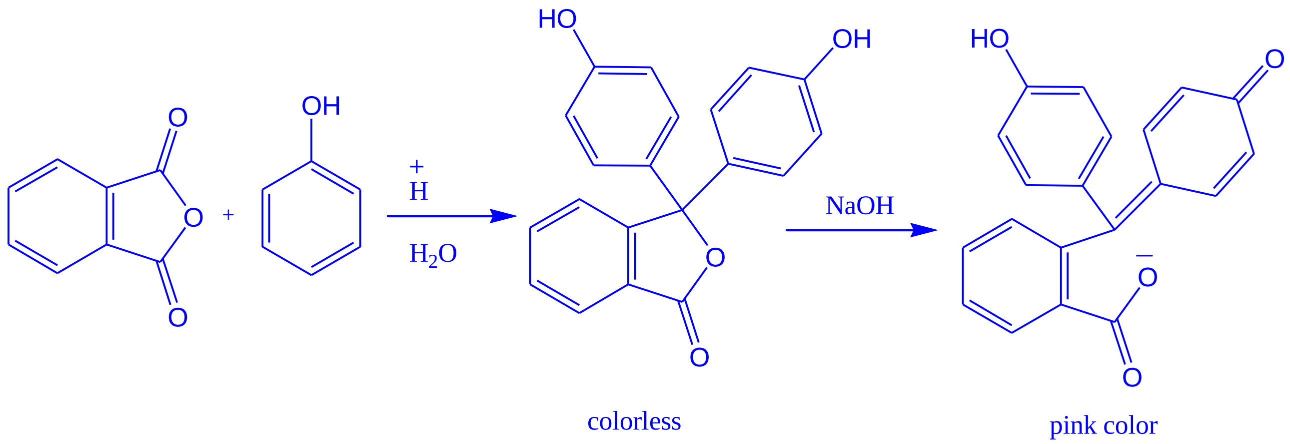
Place 0.2 g of the unknown in a dry test tube and dissolve in 1ml of conc.H_2SO_4 . Add a few crystals of sodium nitrite. Immediately a blue green or blue violet color is formed. Dilute the contents with water, the color changes to red which turns blue on dilution with sodium hydroxide solution. Color formation is observed due to the production of a salt of indophenols.



Only those phenols possessing free a para position respond to this test.

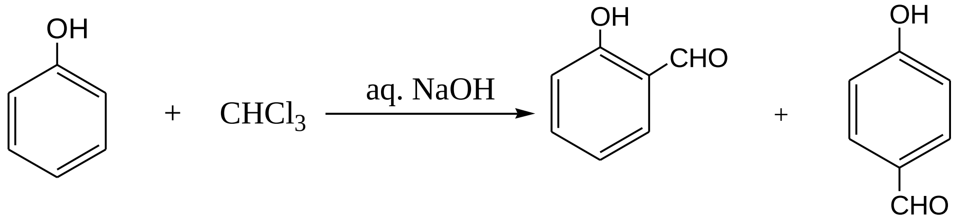
3- Phthalein test (×)

Heat 0.2 g each of the unknown and phthalicanhudride with only 2 drops of conc. sulfuric acid in a test tube for 1 min. Cool and carefully add the contents to 10% sodium hydroxide solution taken in a beaker. Characteristic color are obtained**.**



4-Reimer-Tiemman reaction (×)

Treatment of phenol with chloroform and aqueous sodium hydroxide solution introduces an aldehyde group (-CHO) into the aromatic ring at the ortho- or para-position:



o-hydropxybenzaldehyde
(salicylaldehyde)
(main product, 80%)

p-hydroxybenzaldehyde
(by-product, 20%)

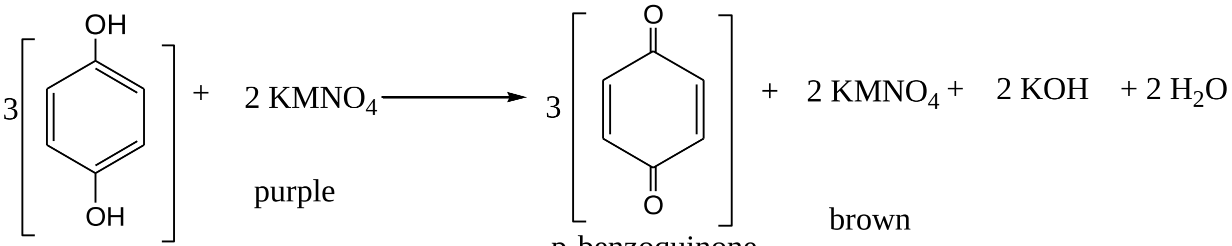
Procedure

To about 0.2 g of the phenol add1 ml of 30% sodium hydroxide solution and 1 ml of chloroform, heat on water bath, and observe the colour of the aqueous layers:

Compound	Colour
Phenol	yellow or no colour
Resorcinol	red colour
α-naphthol	dark green
β-naphthol	deep blue that turns to green
o-cresol	deep orange
m-cresol	pale orange
p-cresol	Yellow
Hydroquinone	deep brown

5- *Reduction of potassium permanganate*

Phenols reduce potassium permanganate solution and undergo oxidation to quinones. The manganese is reduced from +7, which gives a purple solution, to +4, which is brown. This test is highly successful with dihydroxylatd phenols than phenol itself.



hdroquinone

p-benzoquinone

Procedure

Add 0.1 g or 0.2 ml (3-4 drops) of the compound to 2 ml of water or ethanol. Add 2% aqueous potassium permanganate solution drop by drop with shaking until the purple colour of the permanganate persists. If the permanganate color is not changed in 0.5-1 minutes, allow the mixture to stand for 5 minutes with occasional vigorous shaking. The disappearance of the purple color and the formation of a brown suspension, which is manganese (II) oxide, at the bottom of the test tube is a positive result for the presence of phenols.

1- Why phenols are stronger than alcohols as acidic compounds?

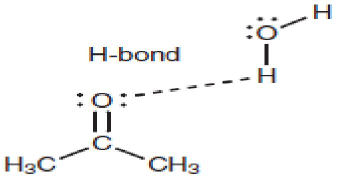
EXPERIMENT (15)

DETACTION OF ALDEHYDES AND KETONES

***Carbonyl group*:**

Both aldehydes and ketones contain a carbonyl group (C=O). The substituents attached to the carbonyl group determine whether it is an aldehyde or a ketone, and whether it is aliphatic or aromatic. The geometry of the carbonyl group is planar with bond angles of 120°. The carbon and oxygen atoms of the carbonyl group are *sp*2 hybridized and the double bond between the atoms is made up of a strong σ bond and a weaker π bond. The carbonyl bond is shorter than a C−O single bond (1.22 Å vs. 1.43 Å) and is also stronger since two bonds are present as opposed to one (732 kJ mol−1 vs. 385 kJ mol−1). The carbonyl group is more reactive than a C−O single bond due to the relatively weak π bond. The carbonyl group is polarized such that the oxygen is slightly negative and the carbon is slightly positive. Both the polarity of the carbonyl group and the presence of the weak π bond explain much of the chemistry and the physical properties of aldehydes and ketones. The polarity of the bond also means that the carbonyl group has a dipole moment.

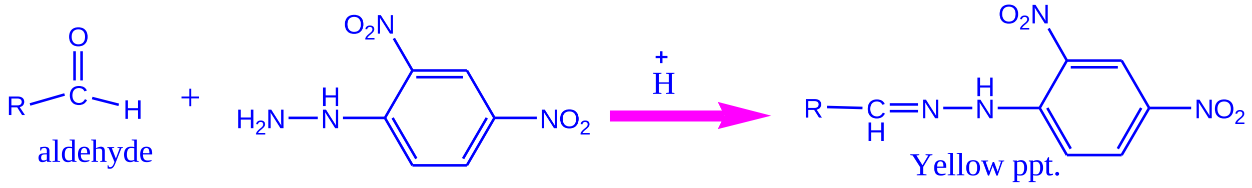
Due to the polarity of the carbonyl group, aldehydes and ketones have a nucleophilic oxygen center and an electrophilic carbon center as shown for propanal. Therefore, nucleophiles react with aldehydes and ketones at the carbon center, and electrophiles react at the oxygen center.

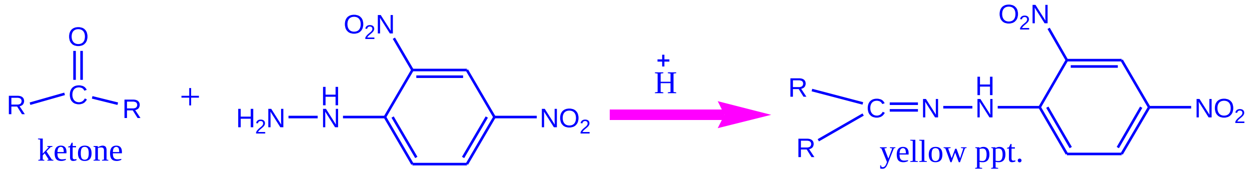


Intermolecular hydrogen bonding of a ketone with water

Detections:

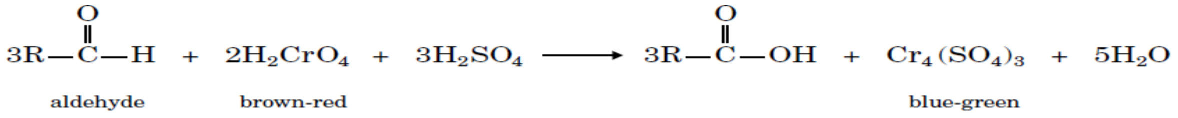
a- **2,4-Dinitrophenylhydrazine test.** All aldehydes and ketones give an immediate precipitate with 2,4-dinitrophenylhydrazine reagent. This reaction is general for both these functional groups. The color of the precipitate varies from yellow to red.



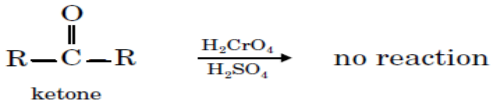


Procedure: Place 5 drops of the substance into a clean, dry test tube, add 20 drops of the 2, 4-dinitrophenylhydrazine reagent to it. If no precipitate forms immediately, heat for 5 min. in a warm water bath (60°C); cool. Record your observations.

b- **Chromic acid test** Aldehydes are oxidized to carboxylic acids by chromic acid; ketones are not oxidized. A positive test results in the formation of a blue-green solution from the brown-red color of chromic acid.



$$\underset{\text{aldehyde}}{3R-\overset{\overset{O}{\|}}{C}-H} + \underset{\text{brown-red}}{2H_2CrO_4} + 3H_2SO_4 \longrightarrow 3R-\overset{\overset{O}{\|}}{C}-OH + \underset{\text{blue-green}}{Cr_4(SO_4)_3} + 5H_2O$$

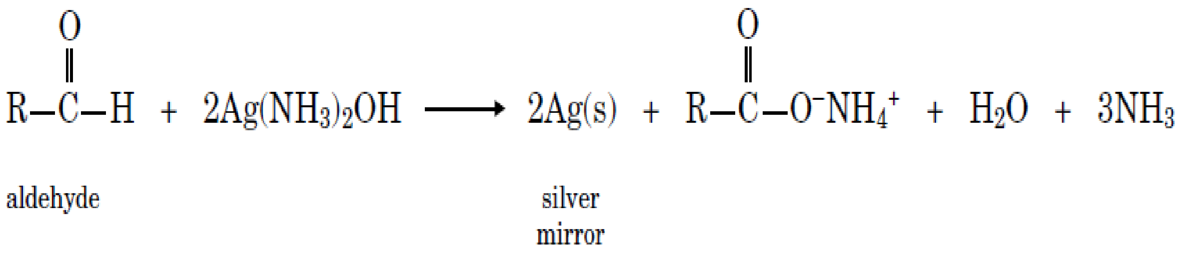


$$\underset{\text{ketone}}{R-\overset{\overset{O}{\|}}{C}-R} \xrightarrow[H_2SO_4]{H_2CrO_4} \text{no reaction}$$

Procedure: 1-Place 5 drops of the unknown in a test tube. 2-Add to the test tube1ml of acetone. 3-Add 3-4 drops of chromic acid. 4- Let the tube for 10 minutes and observe the change.

c- **Tollens test**

Most aldehydes reduce Tollens' reagent (ammonia and silver nitrate) to give a precipitate of silver metal. The free silver forms a silver mirror on the sides of the test tube. (This test is sometimes referred to as the "silver mirror" test.) The aldehyde is oxidized to a carboxylic acid.



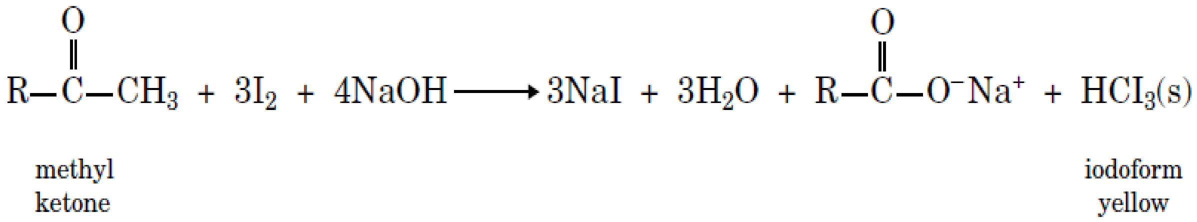
$$R-\overset{\overset{O}{\|}}{C}-H + 2Ag(NH_3)_2OH \longrightarrow 2Ag(s) + R-\overset{\overset{O}{\|}}{C}-O^-NH_4^+ + H_2O + 3NH_3$$

Procedure:

Place 5 drops of the substance into a, dry test tube. Dissolve the compound in ether by adding this solvent dropwise until a homogeneous solution is obtained. Then, add 2 mL (approx. 40 drops) of the prepared Tollens' reagent and mix by sharply tapping the test tube with your finger. Place the test tube in a 60°C water bath for 5 min. Remove the test tubes from the water and look for a silver mirror. If the tube is clean, a silver mirror will be formed; if not, a black precipitate of finely divided silver will appear. Record your results. (mix 5 mL of Tollens' solution A with 5 mL of Tollens' solution B. To the silver oxide precipitate which forms, add (dropwise, with shaking) 10% ammonia solution until the brown precipitate just dissolves. Avoid an excess of ammonia.

d- Iodoform test.

Methyl ketones give the yellow precipitate iodoform when reacted with iodine in aqueous sodium hydroxide.



$$R-\overset{\overset{O}{\|}}{C}-CH_3 + 3I_2 + 4NaOH \longrightarrow 3NaI + 3H_2O + R-\overset{\overset{O}{\|}}{C}-O^-Na^+ + HCI_3(s)$$

Procedure: Place 5 drops of the sample into a clean, dry test tube. Add to the test tube 2mL of water. If the compound is not soluble, add dioxane (dropwise) until the solution is homogeneous. Add to the test tube (dropwise) 2mL of 6 M NaOH; tap the test tube with your finger to mix. The mixture is warmed in a 60°C water bath, and the prepared solution of I2-KI test reagent is added dropwise (with shaking) until the solution becomes brown (approximately 25 drops). (If the color fades, add more I2-KI test reagent until the dark color persists for 2 min. at 60°C.) Add 6 M NaOH (dropwise) until the solution becomes colorless. Keep the test tubes in the warm water bath for 5 min. Remove the test tubes from the water, let cool, and look for a yellow precipitate. Record your observations. The formation of the yellow precipitate tends to be slow.

e- Sodium nitroprusside test

Methyl ketones give positive test with the sodium nitroprusside solution

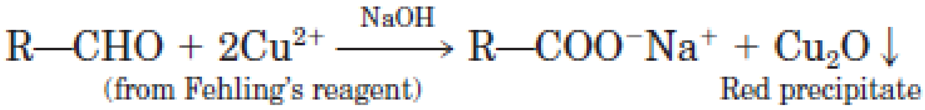
$$Na_2[Fe(CN)_5NO] + CH_3COR \longrightarrow Fe(CN)_5NOCH_2COR$$

Add some drops of sodium nitroprusside solution in water to 5 drops of the sample, and then add NaOH solution, formation red color indicates the presence of methyl ketones.

f- Fehling test

The reagent is made just prior to use by mixing equal volumes of Fehling's solution I, containing copper (II) sulfate, with solution II, containing tartaric acid and alkali. The copper, present as a deep blue complex anion, if reduced by an aldehyde from the copper (II) to the copper (I) state, precipitates as red copper (I) oxide. If the initial step in the reaction involved oxidation of the aldehydic group of the aldose to a carboxyl group, a ketose should not reduce Fehling's solution, or at least should react less rapidly than an aldose, The aldehyde reduces the cupric compound in the alkaline solution to cuprous oxide.

***Procedure*:** Mix 1ml of Fehling's Solution A with 1ml of Fehling's Solution B, and then add 10mg of unknown, warm in boiling water, the formation of red color ppt. indicate the presence of an aldehyde compound.

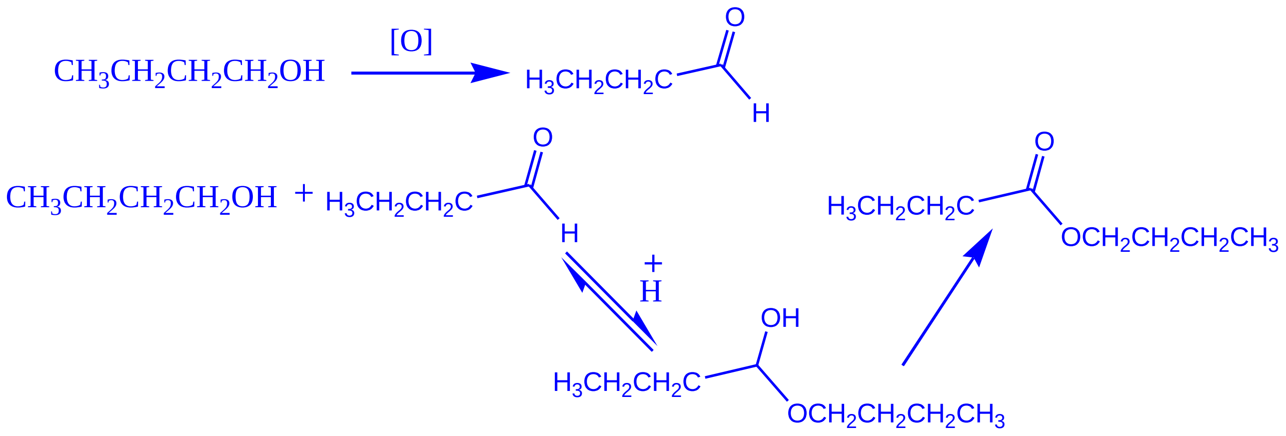


$$\underset{\text{(from Fehling's reagent)}}{R{-}CHO + 2Cu^{2+}} \xrightarrow{NaOH} R{-}COO^-Na^+ + \underset{\text{Red precipitate}}{Cu_2O\downarrow}$$

EXPERIMENT (16)

PREPARATION OF BUTERALDEHYDE (ALDEHYDE)

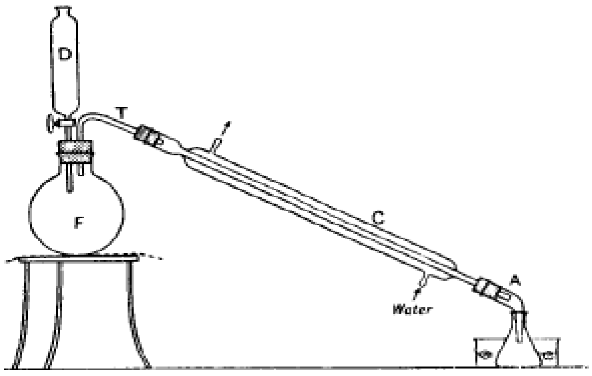
Simple aldehydes may be obtained in reasonably good yield by oxidation of the corresponding primary alcohols with sodium dichromate in dilute sulphuric acid solution(e.g.butyraldehyde).To avoid further oxidation responding acid, the aldehyde is removed as possible by distillation through fractionating column .The main by-product is an ester which arises as the result of the oxidation of an intermediately formed hemiacetal.



Sodium dichromate is used instead of the potassium salt because it is far more soluble in water, and is not precipitated from its aqueous solution by addition of the ethanol. It is also cheaper than the potassium salt, but has the disadvantage of being deliquescent

Procedure:

Dissolve 56 g(0.188 mol) of sodium dichromate dehydrate in 300 ml of water and add cautiously, with stirring, 40 ml of conc. H_2SO_4. Place 41 g(51ml, 0.55mol) of butan-1-ol together with a few small chips of boiling stones in the flask, heat the butan-1-ol to boiling and run in the dichromate solution via the dropping funnel during about 20 min. The oxidation to buteraldehyde proceeds with the evolution of heat, but it is necessary to continue to heat the flask so that the mixture boils vigorously to maintain steady distillation. The temperature at the top of the flask, however, should not exceed 80-85°C. When the entire oxidizing agent has been added, continue heating the mixture for 15 min. and collect all that passes over bellow 90°C. Separate the water from the distillate and dry the residue for 30-60 minutes with 3-4g of anhydrous sodium sulphate. Meanwhile detach the fractionating column from the apparatus and distillate the product slowly (1-2 drops per second) through the column and collect as fairly pure buteraldehyde all that distillate below 76 °C. The yield is 13g(32%). Pure buteraldehyde boils at 74.5°C.

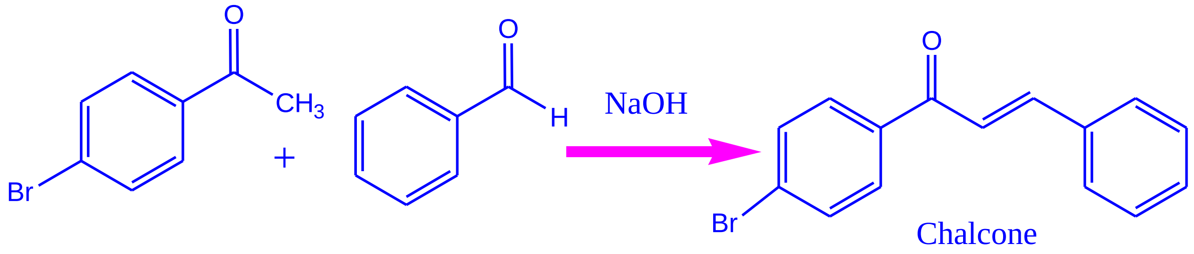


Apparatus for preparation of buteraldehyde

EXPERIMENT (17)

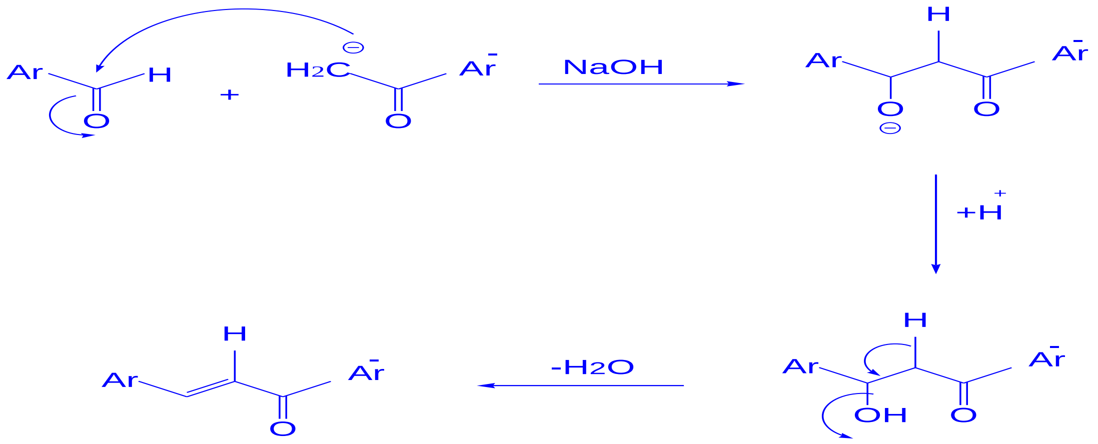
PREPARATION OF CHALCONE (KETONE)

Aldol condensations represent an important class of carbon-carbon bond formationreactions both in nature and in synthetic chemistry. Compounds called chalconescan be prepared by the aldol condensation of an aromatic ketone and an aldehyde. Ina chalcone, two aromatic rings are joined by a 3-carbon α-β -unsaturated carbonyl systemIn this experiment, a benzaldehyde and a derivative ofacetophenone are treated withbase to form a chalcone.



This crossed-aldol condensation does not form mixtures because the substitutedbenzaldehydes have no α-hydrogens, and therefore cannot form an enolate The benzophenonederivatives can form enolates, and they will react with the aldehyde morerapidly than with themselves because aldehydes are more electrophilic than ketones. As is true of most aldol condensations involving aromatic aldehydes, the aldol addition products readily undergo dehydration to give α-β unsaturated carbonyl componds. The double bond formed is conjugated with both the carbonyl group and thearomatic ring. This step is irreversible under the reaction conditions and serves todrive the equilibrium toward the formation of the products. The extensive conjugationof the products cause them to absorb light in the visible region, lending them ayellow color.

Mechanism:



Procedure:

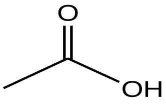
Chalcone can synthesis by dissolving 0.01 mol of the acetophenone in 10ml of ethanol, and added to the solution of an appropriate benzaldehyde 0.01mol in ethanol 20 ml and (10 ml) of 4% ethanolic sodium hydroxide. Heat with stirring at room temperature for (10 min.) until the formation of pale yellow crystals of chalcone, and Cool in an ice-water bath until crystal formation is complete. Chalcone crystals were separated by suction filtration.

EXPERIMENT (18)

DETECTION OF CARBOXYLIC ACIDS

A carboxylic is an organic compound that contains a carboxyl group (COOH). The general formula of a carboxylic acid is R−COOH

Carboxylic acids are structurally like aldehydes and ketones in that they contain the carbonyl group. However, an important difference is that carboxylic acids contain a hydroxyl group attached to the carbonyl group. .

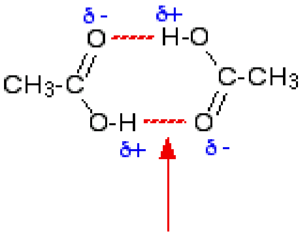


The carboxylic acid group

This combination gives the group its most important characteristic; it behaves as an acid. As a family, carboxylic acids are weak acids that ionize only slightly in water.

Physical properties:

The boiling points of carboxylic acids increases as the molecules get bigger. Carboxylic acids have even higher boiling points than corresponding alkanes and alcohols. Carboxylic acids, similar to alcohols, can form hydrogen bonds with each other. However, unique to carboxylic acids, hydrogen bonding can occur between two molecules to produce a dimmer.



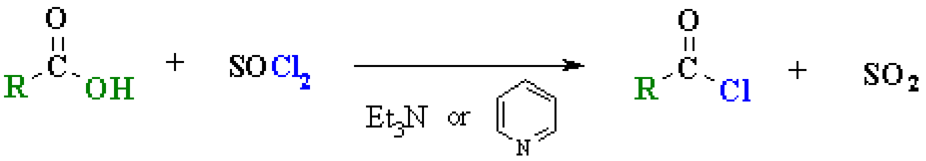
Hydrogen bond between the fairly positive hydrogen atom and a lone pair on the fairly negative oxygen atom.

The presence of dimmers increases the strength of the van der Waals dispersion forces, resulting in the high boiling points of carboxylic acids.

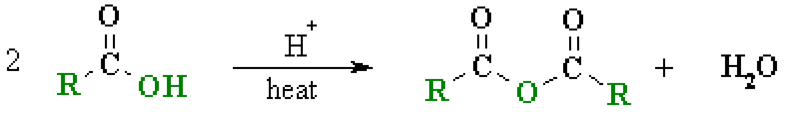
Carboxylic acids are classified as weak acids. Typically, the pK+'s of a carboxylic acid is approximately 5. Even though they are categorized as 'weak' acids, having a pK+'s greater than 1, carboxylic acids are much stronger acids than alcohols. This is because the product of ionization is a resonance stabilized carboxylate ion, so the acid-base equilibrium is shifted to favor ionization when compared to alcohols.

Chemical reactions (Reactivity):

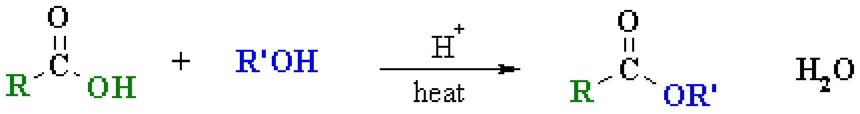
1- Preparation of Acyl Chlorides



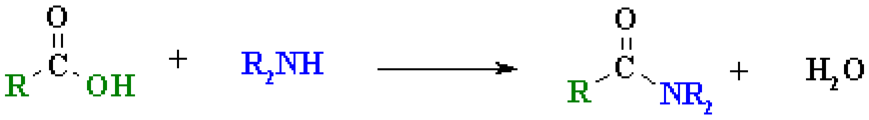
2- Preparation of Acid Anhydrides



3- Preparation of Esters



4-Preparation of amide



Detections:

1– Litmus paper test. Dissolve 0.1g of unknown in minimum volume of water. With a glass rod apply a drop on a blue litmus paper. A change to red color indicates the substance to be acidic.

2– Sodium bicarbonate test. Place 0.2g of the unknown in a test tube and add 1ml of 5% aqueous sodium bicarbonate solution. Appearance of effervescence (or slow up and down movement of particles) indicates the presence of an acid.

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

3- Esterfication. Into clean, dry test tube, add 10 drops of liquid carboxylic acid or 0.1 g of solid carboxylic acid and 10 drops of alcohol. Add 5 drops of concentrated sulfuric acid to the test tube and mix the contents thoroughly by sharply tapping the test tube with your finger. Place the test tubes in a warm water bath at 60°C for 15 min. Remove the test tube from the water bath, cool, and add 2 mL of water to it. Note that there is a layer on top of the water in the test tube. With a pipette, take a few drops from this top layer and place on a watch glass. Note the odor.

$$\mathrm{RCOOH + R'OH \longrightarrow RCOOR' + H_2O}$$

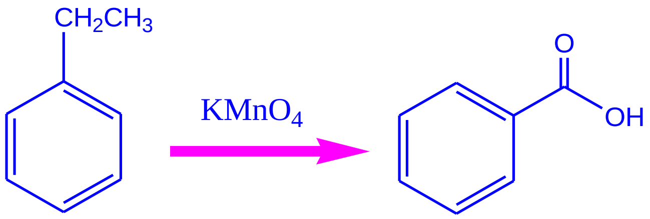
4– Iodate-iodide test

Place (4-5) drops of carboxylic acid in the test tube, add 2ml of 2% KI and 2ml of 4%KIO_3, warm the solution in water bath for 1-2 minutes, cool and add 3 drops of starch solution, violet color appearance indicates the presence of an acid.

$$\mathrm{5KI + KIO_3 + 6RCOOH \longrightarrow 3I_2 + 6RCOOK + 3H_2O}$$

EXPERIMENT (19)

PREPARATION OF BENZOIC ACID



Benzoic acid is the simplest of the aromatic carboxylic acids, a family of organic compounds containing the carboxyl (-COOH) group. It occurs in the form of white crystalline needles or thin plates. Many naturally occurring plants contain benzoic acid, including most types of berries and the natural product called gum benzoin, a plant common to the islands of Java, Sumatra, and Borneo.

More than half of all the benzoic acid produced in the United States is used in the manufacture of various polymeric products, primarily the family of plastics known as the polyvinyl acetates (PVAs). The PVAs, in turn, *are used as adhesives, caulks, sealants, and coatings for paper, film, and plastic foil*. About a quarter of all benzoic acid is converted to its sodium and potassium salts, sodium benzoate (C_6H_5COONa) and potassium benzoate (C_6H_5COOK), for use as food preservatives. Sodium benzoate and potassium benzoate are now the most widely used food preservatives in the world. They are added to a host of products, such as soft drinks and fruit juices, jams and jellies, baked goods, and salad dressings. They are also added to a number of non-food products such as mouthwashes, toothpastes, cosmetic creams, and deodorants.

Procedure:

1- In round bottomed flask dissolve 5g of anhydrous sodium carbonate in 150ml of D.W. then add 10g of potassium permanganate $KMnO_4$ and 3g of ethyl benzene .

2 – Reflux the mixture for 1.5 h. to oxidize ethyl benzene to sodium benzoate and reduction of $KMnO_4$ to MnO_2 which absorb high quantity of benzoate.

3 – Cool the mixture; add 50ml of conc. HCl which to precipitation of benzoic acid (How).
4 – Add 3g of sodium sulfite slowly with shaking and heating to complete dissolving MnO_2.
5 – Cool and filter the product by Buchner funnel, then recrystallize the product with small portion of water.