

**Practical Organic Chemistry 1**  
**Second Stage**  
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## **Physical constants for organic compounds**

### **1- Melting point**

The melting point of a crystalline solid is the temperature at which the solid begins to change into liquid under a pressure of one atmosphere. For pure substances, the change from the solid to the liquid state is quite sharp (within 0-2 °C); hence the temperature is valuable for purposes of identification. Moreover, the melting point is considerably influenced by the presence of other substances, and it is therefore an important criterion of purity.

### **Experimental determination of the melting point**

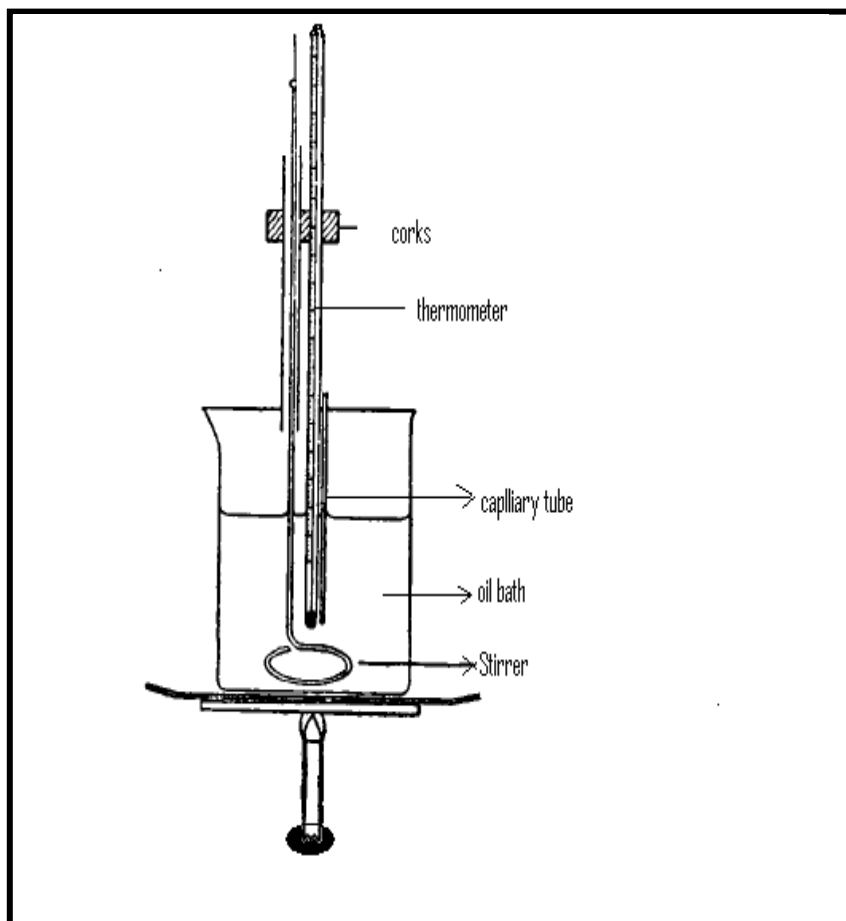
A pure crystalline organic compound has, in general, a definite and sharp melting point, that is, the melting point range (the difference between the temperature at which the collapse of the crystals is first observed and the temperature at which the sample becomes completely liquid) does not exceed about 0-2 °C. The presence of small quantities of miscible, or partially miscible, impurities will usually produce a marked increase in the melting point range and cause the melting to occur at a temperature lower than the melting point of the pure substance. The melting point is therefore a valuable criterion of purity for an organic compound.

A sharp melting point is usually indicative of the high purity of a substance. There are, however, some exceptions. Thus a eutectic mixture of two or more compounds, it is reasonable to regard a compound as pure when it melts over a range of about 0-2 °C (or less) and the melting point is unaffected by repeated fractional crystallization.

In addition to the use of a melting point determination as a criterion of purity, an equally valuable application is for the identification of organic compounds. If the melting point is known within one degree, the major proportion of possible substances is immediately eliminated from consideration. The study of the general chemical properties of the compound and a mixed melting point determination will largely establish the identity of the compound.

## The experimental method

The experimental method in most common use is to heat a small amount (about 1 mg) of the substance in a capillary tube attached to a thermometer which is immersed in a suitable bath of liquid, and to determine the temperature at which melting occurs.



Melting point apparatus

## 2-Boiling point (b.p.)

The vapor pressure of a liquid increases with rising temperature. When the vapor pressure becomes equal to the *total* pressure exerted on the surface of a liquid, the liquid boils. So, boiling point of a liquid may be defined as the temperature at which the vapor pressure of the liquid is equal to the external pressure Exerted at any point upon the liquid surface. This external pressure may be exerted by atmospheric air, by other gases, by vapor and air, etc. The boiling point at a pressure of 760 mm. of mercury, or one standard atmosphere,

may be termed the normal boiling point. The range of the boiling point should not be exceed 5 °C

### **Experimental determination of the boiling point**

Siwoloboff method: Two tubes, closed at one end, are required; one, an ordinary melting point capillary, and the other, having diameter longer than the first one. A small quantity of the liquid, 0.25-0.5 ml (depending upon the boiling point), is placed in the wider tube, and the capillary tube, with sealed end uppermost, is introduced into the liquid. The tube is then attached to the thermometer by a rubber band (Figure 2), and the thermometer is immersed in an oil bath. As the bath is gradually heated there will be a slow escape of air bubbles from the end of the capillary tube, but when the boiling point of the liquid is attained, a rapid and continuous escape of air bubbles will be observed. The reading of the thermometer when a rapid and continuous stream of air bubbles first emerges from the capillary tube is the boiling point of the liquid. Unless the temperature is raised very slowly in the vicinity of the boiling point of the liquid, the first determination may be slightly in error. A more accurate result is obtained by removing the source of heat when the rapid stream of bubbles rises from the end of the capillary tube ; the speed at which bubbles are given off will slacken and finally, when the last bubble makes its appearance and exhibits a tendency to suck back, the thermometer is read immediately. This is the boiling point of the liquid because it is the point at which the vapor pressure of the liquid is equal to that of the atmosphere.

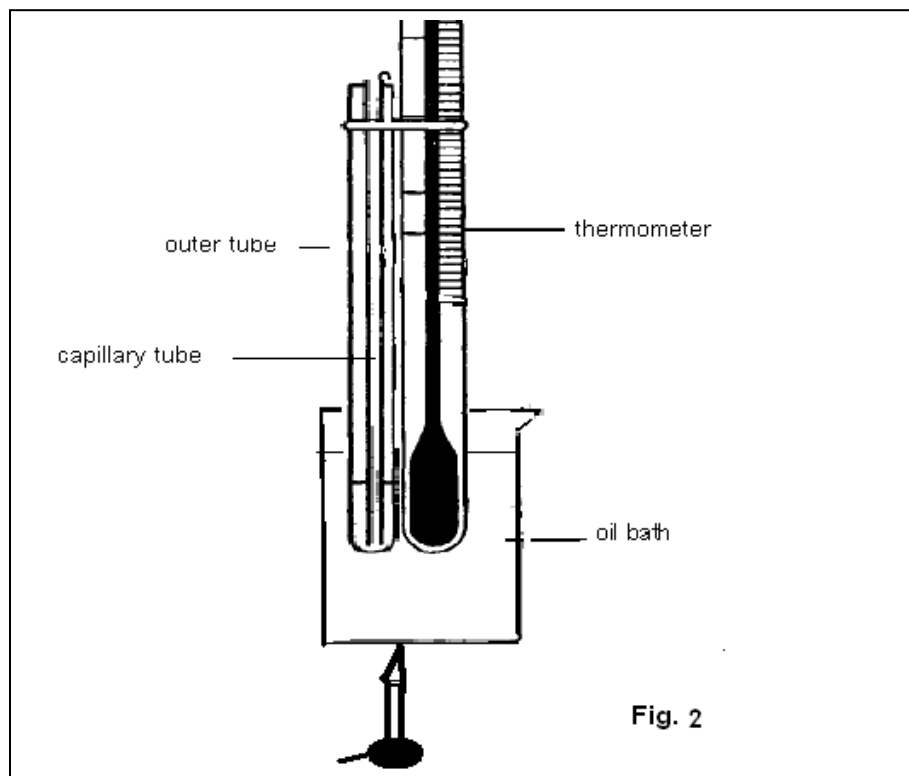


Figure 2: Boiling point apparatus

### **Purification of solid organic compounds by crystallization**

Solid organic compounds when isolated from organic reactions are seldom pure; they are usually contaminated with small amounts of other compounds (impurities) which are produced along with the desired product. The purification of impure crystalline compounds is usually effected by crystallization from a suitable solvent or mixture of solvents.

The purification of solids by recrystallization is based upon differences in their solubility in a given solvent or mixture of solvents between the product and the impurities.

### **The recrystallization process consists**

1. Dissolving the impure substance in some suitable solvent at or near the boiling point.
2. Filtering the hot solution from particles of insoluble material and dust.
3. Allowing the hot solution to cool thus causing the dissolved substance to crystallize out.
4. Separating the crystals from the supernatant solution (or mother liquor). The resulting solid, after drying, is tested for purity (usually by a melting point determination,) and if found impure, it is again recrystallized from fresh solvent. The process is repeated until the pure compound is obtained; this generally means until the melting point is unchanged.

### **The most desirable properties of a solvent for recrystallization are:**

1. A high solvent power for the substance to be purified at elevated temperatures and a comparatively low solvent power at the laboratory temperature or below.
2. It should dissolve the impurities readily or to only a very small extent.
3. It should yield well-formed crystals of the purified compound.
4. It must be capable of easy removal from the crystals of the purified compound, *i.e.*, possess a relatively low boiling point. It is assumed, of course, that the solvent does not react chemically with the substance to be purified. If two or more solvents appear to be equally suitable for the recrystallization, the final selection will depend upon such factors as ease of manipulation, inflammability and cost.

## Common solvents for recrystallization

SOLVENT	B.P.	REMARKS
Water (distilled)	100°	To be used whenever suitable.
Diethyl ether	35°	Inflammable; avoid wherever possible.
Acetone	56°	Inflammable; should preferably be dried before use.
Chloroform	61°	Non-inflammable; vapour toxic.
Methyl alcohol	64.5°	Inflammable; poisonous.
Carbon tetrachloride	77°	Non-inflammable; vapour toxic.
Ethyl acetate	78°	Inflammable.
Methylated (industrial) spirit	77-82°	Inflammable.
Rectified spirit (95% C <sub>2</sub> H <sub>5</sub> OH)	78°	Inflammable.
Ethyl alcohol (absolute)	78°	Inflammable.
Benzene	80°	Inflammable.
Light petroleum (petroleum ether)	40-60°	Inflammable.*
Acetic acid (glacial)	118°	Not very inflammable; pungent vapours.

The choice of solvent- cannot usually be made on the basis of theoretical considerations alone but must be experimentally determined,

### The solvent is unsuitable in the following cases

1. If the sample dissolves easily in 1 ml of cold solvent or upon gentle warming, the solvent is unsuitable.
2. If the substance does not dissolve on heating; the substance is regarded as sparingly soluble in that solvent, and another solvent should be sought.
3. If crystals do not separate, even after scratching for several minutes and cooling in an ice-salt mixture, the solvent is rejected.

### Removal of traces of coloring matter and resinous products use of decolorizing carbon

The crude product of an organic reaction may contain a colored impurity. Upon recrystallization, this impurity dissolves in the boiling solvent and is partly adsorbed by the crystals as they separate upon cooling, yielding a coloured product. These impurities can be removed by boiling the substance in solution with a little decolorizing charcoal (also known as bone black or bone charcoal) for 5-10 minutes, and then filtering the solution while hot. The decolorizing charcoal adsorbs the colored impurity and holds back resinous,

finely-divided matter, and the filtrate is usually free from extraneous color, and therefore deposits pure crystals

### Experimental details for recrystallization

1-Erlenmeyer flask is very suitable for recrystallization and must not be used opened beaker.

2- Filtration of the hot solution.

The hot solution must be rapidly filtered before undue cooling has occurred. This is usually done through a fluted filter paper (for preparation, see Figure 3, a, b, c and d)

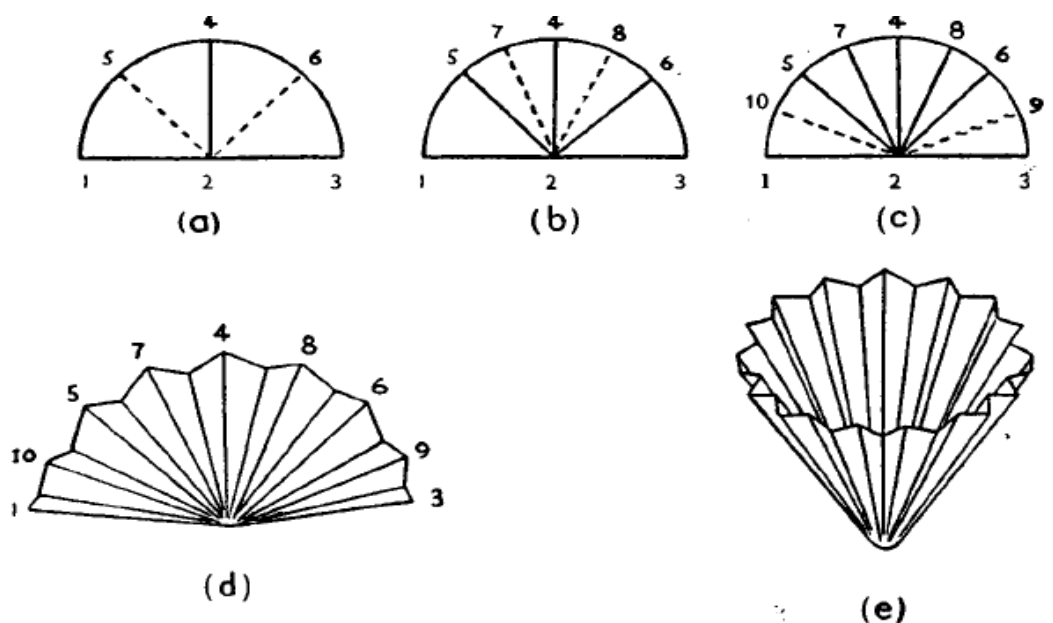


Figure 3: Preparation of a fluted filter paper

### 3-Filtration with suction (a Buchner apparatus)

The filtration of cold solutions will now be considered; this operation is usually carried out when it is desired to separate a crystalline solid from the mother liquor in which it is suspended. When substantial quantities of a solid are to be handled, a Buchner funnel of convenient size is employed. The ordinary Buchner apparatus is shown in Figure 4.



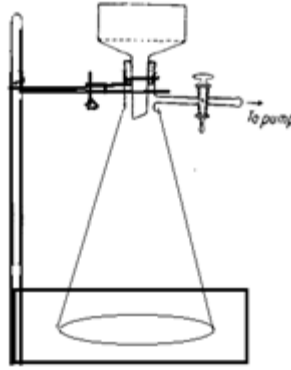


Figure 4: Buchner apparatus

### Fractional distillation

The aim of distillation is the separation of a volatile liquid from a non-volatile substance or, more usually, the separation of two or more liquids of different boiling point. The latter is usually termed **fractional distillation**.

The theoretical treatment of fractional distillation requires knowledge of the relation between the boiling points, or vapor pressures, of mixtures of the substances and their composition; if these curves are known, it is possible to predict whether the separation is difficult or easy or, indeed, whether it will be possible. At the outset it will be profitable to deal with an **ideal solution** possessing the following properties:

1. There is no heat effect when the components are mixed.
2. There is no change in volume when the solution is formed from its components.
3. The vapor pressure of each component is equal to the vapor pressure of the pure substances multiplied by its mole fraction\* in the solution. The last-named property is merely an expression of Raoult's law, *viz.*, the vapor pressure of a substance is proportional to the number of moles of the substance present in unit volume of the solution, applied to liquid-liquid systems. Thus we may write:

$$p_A = K \cdot X_A \quad (1)$$

Where  $p_A$  is the vapor pressure of the substance and  $X_A$  is its mol fraction in the solution. If  $X_A = 1$ , *i.e.*, we are dealing with the pure substance A, then  $p_A = K = p_A'$ , the vapor

pressure of the pure substance at the given temperature. Substituting this value in equation (1), we have:

$$P_A = P_A' Z_A \quad (2)$$

i.e., the vapor pressure of a component of a solution at a given temperature is equal to the vapor pressure of the pure substance multiplied by its mol fraction in the solution. This is another form of **Raoult's law**.

**The mol fraction** of any constituent in a mixture is defined as the number of moles, or gram molecules, of that constituent divided by the total number of moles, or gram molecules, in the mixture.

### **Simple apparatus for fractionation**

Figure 6 illustrates a set-up for simple fractionation: a Hempel column is shown, but it may be substituted by a modified Hempel, a Vigreux or an all-glass Dufton column. The Hempel column may be filled with *Y* glass rings, iV porcelain Lessing rings, or with porcelain rings. The mixture to be fractionated is placed in a bolt-head flask of convenient size (it should be one third to one half full), a few fragments of porous porcelain added, the column fixed in position, and a water condenser attached to the side arm. The distillate is collected in small flasks or in test-tubes. The bulb of the thermometer should be just below the level of the side arm (Figure 6)

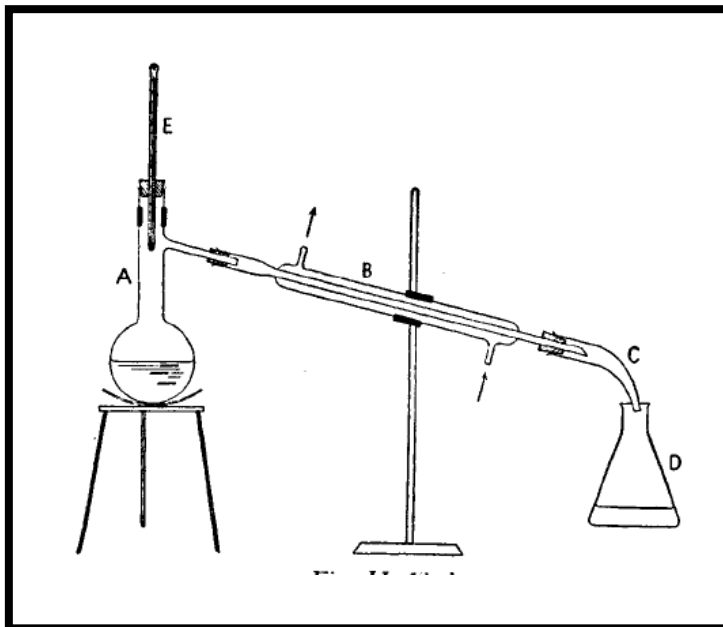


Figure 5: Simple distillations apparatus

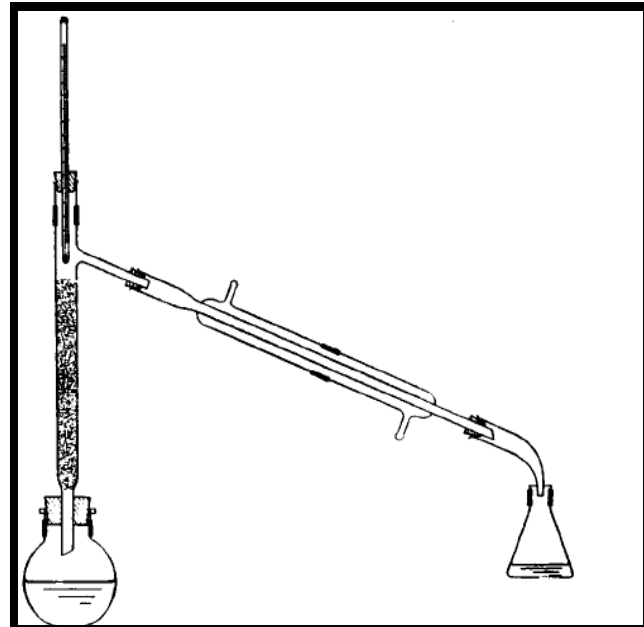


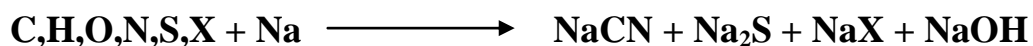
Figure 6: Fractional distillation apparatus

It is advisable to lag the column by wrapping asbestos cloth round it; this will minimize the effect of draughts in producing excessive cooling. Lagging of the column is essential if the boiling point of any of the components exceeds 100. The flask is then heated with a small flame, protected from draughts so as to ensure a uniform heating; an air bath gives better results. The initial heating must not be hurried as owing to the considerable extra condensation which occurs whilst the column is warming up; the latter may easily choke with liquid. Once distillation has commenced, the size of the flame is adjusted so that the liquid passes over at the rate of one drop every two or three seconds. Under these conditions fairly efficient fractionation should be obtained. When the low boiling point fraction has passed over, distillation should cease. The heating is then slowly increased, and a sharp rise in boiling point should occur as the second fraction commences to distil; it is assumed, of course, that the fractionating system is capable of effecting a sharp fractionation of the components of the mixture. If the set-up is inefficient, a relatively large intermediate fraction may be obtained. It is desired to emphasize the fact that the distillation must be conducted slowly; no time is usually saved by distilling rapidly since a second fractionation will then be necessary.

## Qualitative analysis for the elements

### Nitrogen, Sulphur and halogens

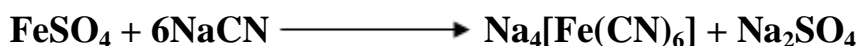
In order to detect these elements in organic compounds, it is necessary to convert them into ionisable inorganic substances so that the ionic tests of inorganic qualitative analysis may be applied. This conversion may be accomplished by several methods, but the best procedure is to fuse the organic compound with metallic sodium (Lassaigne's test). In this way sodium cyanide, sodium sulphide and sodium halides are formed, which are readily identified. Thus, organic compound containing



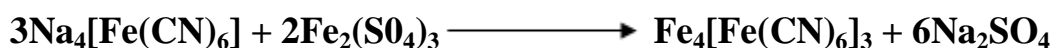
It is essential to use an excess of sodium, otherwise if sulphur and nitrogen are both present sodium thiocyanate, NaCNS, may be produced; in the test for nitrogen it may give a red coloration with ferric iron but no Prussian blue since there will be no free cyanide ions. With excess of sodium the thiocyanate, if formed, will be decomposed:



The filtered alkaline solution, resulting from the action of water upon the sodium fusion, is treated with ferrous sulphate and thus forms sodium ferrocyanide:



Upon boiling the alkaline ferrous salt solution, some ferric ions are inevitably produced by the action of the air ; upon the addition of dilute sulphuric acid, thus dissolving the ferrous and ferric hydroxides, the ferrocyanides reacts with the ferric salt producing ferric ferrocyanide (Prussian blue)



Hydrochloric acid should not be used for acidifying the alkaline solution since the yellow color, due to the ferric chloride formed, causes the Prussian blue to appear greenish. For the same reason, ferric chloride should not be added as is frequently recommended: a sufficient concentration of ferric ions is produced by atmospheric oxidation of the hot alkaline solution. The addition of a little dilute potassium fluoride solution may be

advantageous in assisting the formation of Prussian blue in a readily filterable form. Sulphur, as sulphide ion, is detected by precipitation as black lead sulphide with lead acetate solution and acetic acid or with sodium plumbite solution (an alkaline solution of lead acetate). Halogens are detected as the characteristic silver halides by the addition of silver nitrate solution and dilute nitric acid: the interfering influence of sulphide and cyanide ions in the latter tests are discussed under the individual elements

**The following alternative procedure is recommended and it possesses**

The advantage is the same tube may be used for many sodium fusions. Support a Pyrex test-tube (150 X 12 mm.) vertically in a clamp lined with asbestos cloth or with sheet cork. Place a cube (*circa* 4 mm. side= 0.04 gm) of freshly cut sodium in the tube and heat the latter until the sodium vapor rises 4-5 cm. in the test-tube. Drop a small amount (about 0.05 gm) of the substance, preferably portion wise, directly into the sodium vapor (*CAUTION*: there may be a slight explosion); then heat the tube to redness for about 1 minute. Allow the test-tube to cool, add 3-4 ml of methyl alcohol to decompose any unreacted sodium, then half fill the tube with distilled water and boil gently for a few minutes. Filter and use the clear, colorless filtrate for the various tests detailed below. Keep the test-tube for sodium fusions; it will usually become discolored and should be cleaned from time to time with a little scouring powder.

**Nitrogen**

Pour 2-3 ml of the filtered "fusion" solution into a test tube containing 2 gm of powdered ferrous sulphate crystals. Heat the mixture gently with shaking until it boils, then, without cooling, add just sufficient dilute sulphuric acid to dissolve the iron hydroxides and give the solution an acid reaction. The addition of 1 ml of 5% potassium fluoride solution is beneficial (possibly owing to the formation of potassium ferrifluoride  $K_3[FeF_6]$ ) and usually leads to a purer Prussian blue. A Prussian blue precipitate or coloration indicates that nitrogen is present. If no blue precipitate appears at once, allow to stand for 15 minutes, filter through a small filter and wash the paper with water to remove all traces of colored

solution: any Prussian blue present will then become perceptible in the cone of the filter paper. If in doubt, repeat the sodium fusion, preferably using a mixture of the compound with pure sucrose or naphthalene. In the absence of nitrogen, the solution should have a pale yellow color due to iron salts. If sulphur is present, a *black* precipitate of ferrous sulphide is obtained when the ferrous sulphate crystals dissolve. Boil the mixture for about 30 seconds, and acidify with dilute sulphuric acid; the ferrous sulphide dissolves and a precipitate of Prussian blue forms if nitrogen is present.

### **Sulphur**

1. Acidify 2 ml of the fusion solution with dilute acetic acid, and add a few drops of lead acetate solution. A black precipitate of lead sulphide indicates the presence of sulphur.
2. To 2 ml of the fusion solution add 2-3 drops of a freshly prepared dilute solution (*circa* 0-1%) of sodium nitroprusside  $\text{Na}_2[\text{Fe}(\text{CN})_5\text{NO}]$ . (The latter may be prepared by adding a minute crystal of the solid to about 2 ml of water.). A purple coloration indicates sulphur; the coloration slowly fades on standing.

### **Halogens**

If nitrogen and/or sulphur are present, the addition of silver nitrate to the acidified fusion solution will precipitate silver cyanide and/or silver sulphide in addition to the silver halides. The removal of hydrogen cyanide and/or hydrogen sulphide before precipitation of the silver halides is effected by boiling the fusion solution, just acidified with dilute nitric acid, in an evaporating basin until it has been reduced to half its original volume. Cool, dilute with an equal volume of water and add a few drops of silver nitrate solution. A white or pale yellow precipitate, which darkens rapidly upon exposure to light, indicates the presence of halogen one or more halogens may be present, proceed as follows:

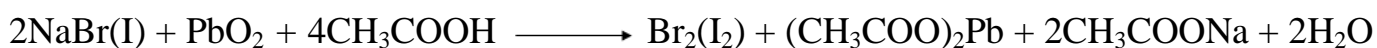
Acidify 1-2 ml of the fusion solution with a moderate excess of glacial acetic acid and add 1 ml of carbon tetrachloride. Then introduce 20% of sodium nitrite solution drop by drop with constant shaking. A purple or violet color in the organic layer indicates the presence of iodine. The reaction is:



This solution may also be employed in the test for bromine. If iodine has been found, add small amounts of sodium nitrite solution, warm slightly and shake with fresh 1 ml portions of carbon tetrachloride until the last extract is colorless; boil the acid solution until no more nitrous fumes are evolved and cool. If iodine is absent, use 1 ml of the fusion solution which has been strongly acidified with glacial acetic acid. Add a small amount of lead dioxide, place a strip of fluorescein paper across the mouth of the tube, and warm the solution. If bromine is present, it will color the test paper rose-pink (eosin)

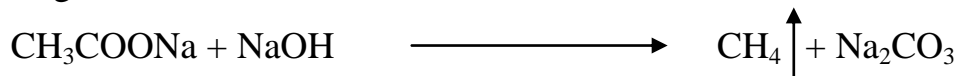
Acidify 1-2 ml of the fusion solution with dilute sulphuric acid, cool, and add 1 ml of carbon tetrachloride. Prepare the equivalent of chlorine water by acidifying 10% sodium hypochlorite solution with one fifth of its volume of dilute hydrochloric acid. Add this solution dropwise (use a dropper) with vigorous shaking to the mixture. If iodine is present, the organic phase first becomes purple in color. As the addition of the chlorine water is continued, the purple color disappears (owing to the oxidation of the iodine to iodate) and, if bromine is present, is replaced by a brown or reddish color. If bromine is absent, the organic layer will be colorless. It is, of course, evident that if the carbon tetrachloride layer remains uncolored, the halogen present is chlorine.

Acidify 1-2 ml of the fusion solution with acetic acid, add a slight excess of pure lead dioxide (say, 0-5 gm) and boil gently until all the iodine and bromine are liberated. Dilute, filter off the excess of lead dioxide, and test for chloride with dilute nitric acid and silver nitrate solution.

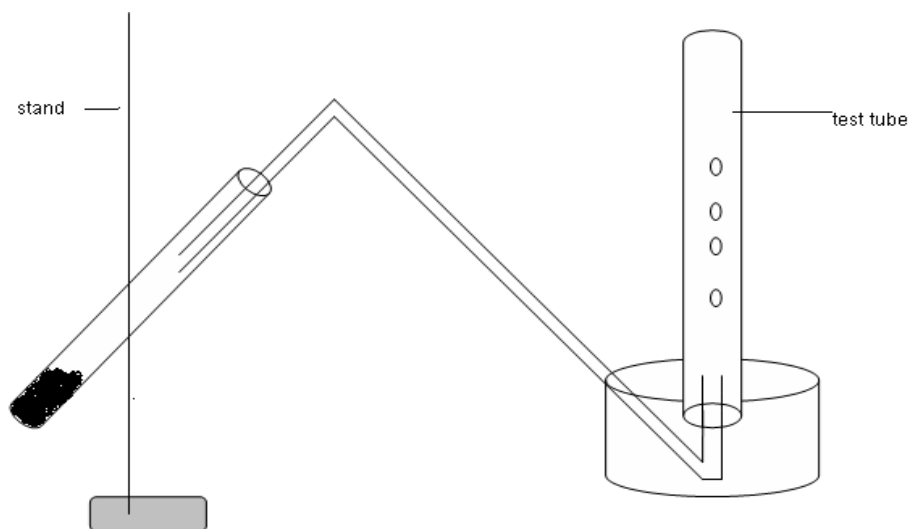


## Reactions and characterization of saturated aliphatic hydrocarbons

**Preparation of methane:** Heating soda lime with sodium hydroxide according to the following reaction:



The following apparatus used for this reaction:



**Figure 7: apparatus used for preparation methane**

Use a sample of purified methane, this carry out the following tests.

### 1. Action of bromine water

Place 1 ml of heptane in each of two test-tubes, and add 3-4 ml of bromine water. Shake the tubes well, and keep one of them in your locker and out of the light. Expose the other tube to bright sunlight {or hold it close to a bright (150-200 watts) electric bulb}. Compare the tubes after about 15 minutes.

### 2. Action of bromine dissolved in a non-aqueous solvent

Repeat experiment 1, but add 0-5 ml of a solution of bromine in carbon tetrachloride (2) to each of the tubes. After 10-15 minutes (or as soon as a change has occurred), examine each of the tubes. Breathe across the mouth of the tube in which a change has taken place and test the vapor with blue litmus paper.



### **3. Action of potassium permanganate solution**

Treat 1 ml of the hydrocarbon with 2 ml of 5% potassium permanganate solution and 1 ml of dilute sulphuric acid. Shake gently for a short time, and observe if the permanganate solution is decolorized.

### **4. Action of concentrated sulphuric acid**

Add 1 ml of the hydrocarbon to 2 ml of concentrated sulphuric acid and shake gently. Observe whether the acid layer is affected in any way.

### **5. Action of concentrated nitric acid**

Add 1 ml of heptane cautiously to 2 ml. of concentrated nitric acid. Note whether any reaction occurs.

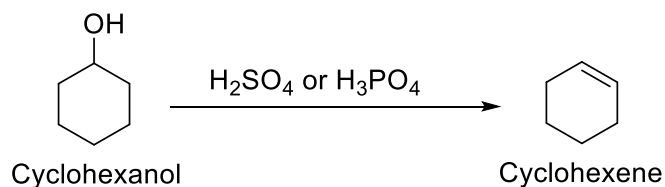
**Notes:** A solution prepared by dissolving 2 gm of bromine in 100 gm of carbon tetrachloride is satisfactory. Carbon tetrachloride is employed because it is an excellent solvent for bromine as well as for hydrocarbons; it possesses the additional advantage of low solubility for hydrogen bromide, the evolution of which renders possible the distinction between decolorization of bromine due to substitution or due to addition

### **Characterization of unsaturated aliphatic hydrocarbons**

Unlike the saturated hydrocarbons, unsaturated aliphatic hydrocarbons are soluble in concentrated sulphuric acid and exhibit characteristic reactions with dilute potassium permanganate solution and with bromine. Nevertheless, no satisfactory derivatives have yet been developed for these hydrocarbons, and their characterization must therefore be based upon a determination of their physical properties (boiling point, density and refractive index).

## Cyclohexene

The alicyclic secondary alcohol, cyclohexanol, may be dehydrated by concentrated sulphuric acid or by 85% phosphoric acid to cyclohexene. It has a higher boiling point (82-83 °C) than cyclohexene and therefore possesses some advantage over the latter in the study of the reactions of unsaturated



### Procedure (Sulphuric acid method):

Place 20 gm of commercial cyclohexanol and 0-6 ml of concentrated sulphuric acid in a 150 or 200 ml round-bottomed or bolt-head flask, add 2-3 chips of porous porcelain, and mix well. Fit the flask with a fractionating column, a Liebig condenser, adapter and filter flask receiver. Heat the flask in an air bath at such a rate that the temperature at the top of the column does not rise above 90 °C; alternatively, an oil bath, heated to a temperature of 130-140 °C, may be used. Stop the distillation when only a small residue remains and the odor of sulphur dioxide is apparent. Transfer the distillate to a small separatory funnel. Saturate the distillate with sodium chloride, add 2 ml of 5% sodium carbonate solution (to neutralize traces of free acid), and shake gently. Allow the two layers to separate, and run off the lower aqueous layer. Pour the crude cyclohexene through the mouth of the funnel into a small dry conical flask, add 3-4 gm of anhydrous calcium chloride or anhydrous magnesium sulphate, shake for 2-3 minutes, and allow standing for 15 minutes with occasional shaking. Decant the dried product through a small funnel supporting a small fluted filter paper into a 25 or 50 ml distilling flask (2), add 2-3 fragments of porous porcelain, and distil. Collect the fraction, b.p. 81-83 °C, in a weighed flask. If appreciable high and low boiling point fractions are obtained, combine these, dry, and redistill. The yield is 12-13 gm.

## **Reactions and characterization of ethylenic hydrocarbons**

Carry out the following tests with the sample of cyclohexene.

### **1. Action of bromine water**

Shake 1 ml. of cyclohexene with 2 ml of bromine water, and note the result.

### **2. Action of bromine in carbon tetrachloride solution**

To 1 ml of cyclohexene add 1-2 ml of the reagent. Observe that no hydrogen bromide is evolved.

### **3. Action of potassium permanganate solution**

Add 1 ml of cyclohexene to 2 ml of 5% potassium permanganate solution and 1 ml of dilute sulphuric acid, and shake. If the reagent is decolorized, add further small quantities.

### **4. Action of concentrated sulphuric acid**

Add cautiously 1 ml of cyclohexene to 2 ml of concentrated sulphuric acid. Shake very gently. Note whether any change in color and in temperature takes place. Cool 1 ml of cyclohexene in ice and add 1 ml of cold, dilute sulphuric acid (2 acid: 1 water), and shake gently until the mixture is homogeneous. Dilute with 2 ml of water; if an upper layer of the alcohol does not separate immediately, introduce a little sodium chloride into the mixture in order to decrease the solubility of the alcohol. Observe the odor. The unsaturated hydrocarbon is thus largely reconverted into the alcohol from which it may be prepared.

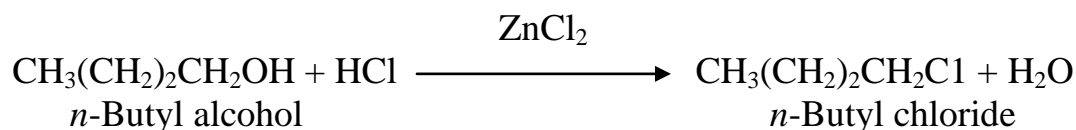
Finally, try to formulate the chemical reactions which occur in the above experiments and submit them to the instructor for comment.

## Alkyl halides

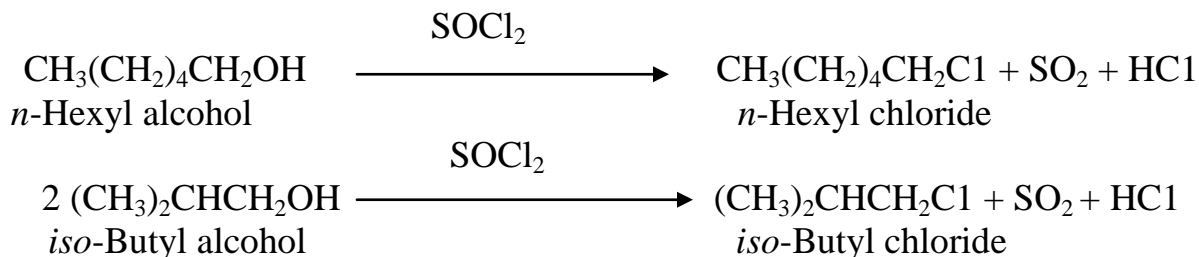
### Alkyl chloride

The chlorides of primary aliphatic alcohols are prepared:

1. By refluxing the alcohol with a mixture of concentrated hydrochloric acid and anhydrous zinc chloride, for example:

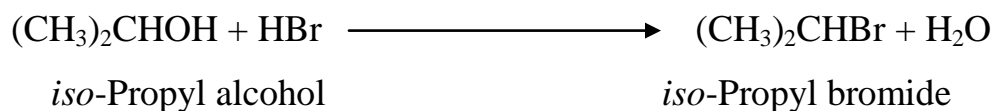


2. By the action of thionyl chloride upon the alcohol alone or mixed with pyridine (to absorb the hydrogen chloride formed in the reaction), for example:

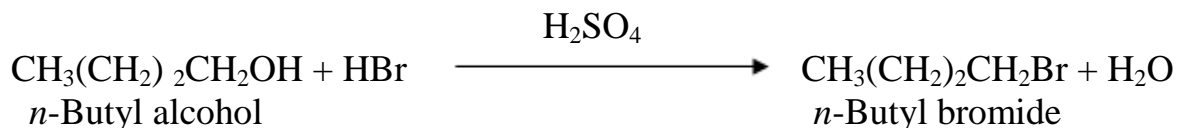


### Alkyl bromide

1. By slow distillation of the alcohol with constant boiling point (48%) hydrobromic acid, for example :

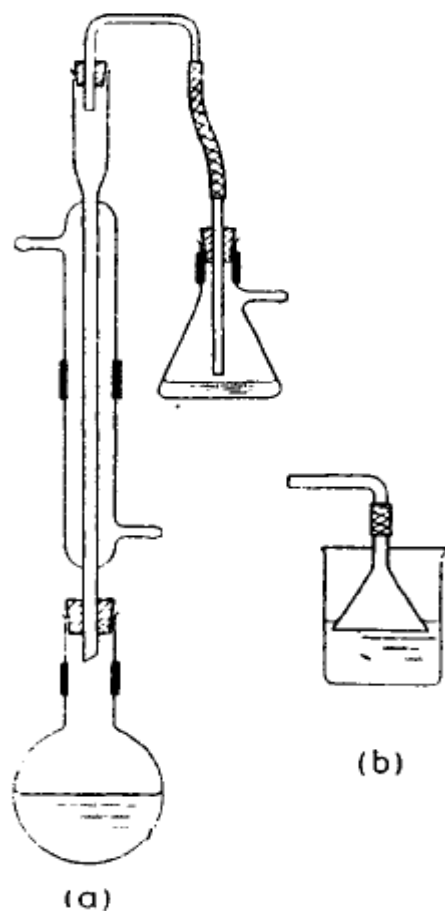


2. By treatment of the alcohol with a mixture of constant boiling point hydrobromic acid and concentrated sulphuric acid; the presence of sulphuric acid results, as a rule, in more rapid reaction and improved yields, a typical example is:



### ***n*-Butyl bromide (KBr-H<sub>2</sub>SO<sub>4</sub> method)**

Dissolve 30 gm of potassium bromide in 50 ml of water in a 350 ml conical flask; *gentle* warming may be necessary. Cool the flask with running water from the tap so that the contents attain room temperature. Add 25 ml of concentrated sulphuric acid slowly and with constant rotation of the flask to ensure thorough mixing ; cool under the tap from time to time and do not allow the temperature to rise above 40 during the addition of the acid. Cool to about 15 °C (under a running water tap), and filter off the precipitated potassium bisulphate using a Buchner funnel and a dry filter flask. Press the precipitate on the filter firmly with the aid of the wide end of a large glass stopper; it is unnecessary to wash the solid with water. Transfer the filtrate to a 250 ml round bottom flask and add 11 gm (14 ml) of *n*-butyl alcohol. Introduce 28 gm (15 ml) of concentrated sulphuric acid slowly and with constant rotation of the contents of the flask; if this operation is carried out carefully, very little hydrogen bromide will be evolved. Add a few small chips of porous porcelain, attach a reflux condenser to the flask, and reflux for 3-4 hours. Remove the reflux condenser, attach a bent tube to the mouth of the flask and set the condenser for downward distillation. Distil slowly on wire gauze until no more oily drops are visible in the condenser. Transfer the distillate to a separatory funnel, remove the lower layer of crude butyl bromide, and discard the upper aqueous layer. Wash the crude halide in the separatory funnel successively with 10-15 ml of concentrated hydrochloric acid (this will remove any unchanged *n*-butyl alcohol), 25 ml of water, 20 ml of 10% sodium carbonate solution and finally with 25 ml. of water: the bromide layer is the lower layer in all cases. Dry the product with 2-3 gm of anhydrous calcium chloride; it is best to leave the halide in contact with the desiccant for about 30 minutes and shake occasionally after an initial shaking of 2-3 minutes. Filter the dried product through a fluted filter paper or a small cotton wool plug supported in a funnel into a dry 50 ml distilling flask, and distil on wire gauze or from an air bath collect the fraction, b.p. 100-103 °C. The yield of *n*-butyl bromide is 18-19 gm



**Figure 8**

In the Figure 8, *a* is for the absorption of a water-soluble gas (hydrogen chloride, hydrogen bromide or sulphur dioxide): it should be noted that the tube is just *above* the level of the liquid in the flask. Alternatively, an inverted funnel (Figure 8, *b*) may be employed for the absorption of gases

## Reactions and characterization of alkyl halide

The following are some of the most important reactions of alkyl halides which will assist in their identification.

### 1. Brillstein's test

This test serves to detect the presence of halogens in many organic compounds. It consists in heating the substance in contact with pure copper oxide in the Bunsen flame: the corresponding copper halide is formed, which, being volatile, imparts an intense green or bluish-green color to the mantle of the flame. Push one end of a length of 20 cm of stout copper wire into a cork (this will serve as a holder); at the other end make two or three turns about a thin glass rod. Heat the coil in the outer mantle of a Bunsen flame until it ceases to impart any color to the flame. Allow the wire to cool somewhat and, while still warm, dip the coil into a small portion of the substance to be tested and heat again in the non-luminous flame. If the compound contains a halogen element, a green or bluish-green flame will be observed (usually after the initial smoky flame has disappeared). Before using the wire for another compound, heat it until the material from the previous test has been destroyed and the flame is not colored. It has been stated that many halogen-free compounds, *e.g.*, certain derivatives of pyridine and quinoline, purines, acid amides and cyano compounds, when ignited on copper oxide impart a green color to the flame presumably owing to the formation of volatile cuprous cyanide. The test is therefore not always trustworthy. The test is not given by fluorides.

### 2. Alcoholic silver nitrate solution

Shake 0.1 gm of the substance with 2 ml of alcoholic silver nitrate solution. Alkyl iodides usually yield silver iodide instantly; alkyl bromides react rapidly, but may require warming; alkyl chlorides give very little precipitate in the cold, but a copious precipitate is obtained by warming on a water bath. The order of reactivity is  $I > Br > Cl$ , and tertiary  $>$  secondary  $>$  primary.

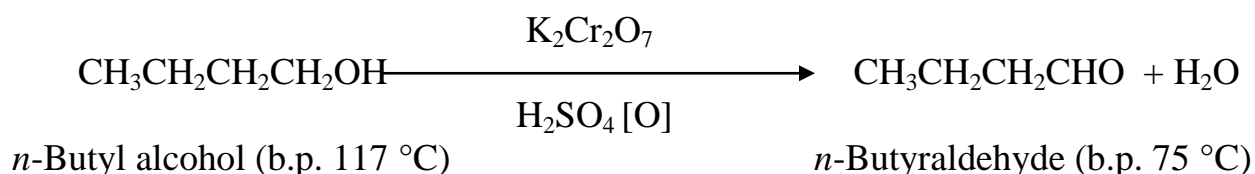
The alcoholic silver nitrate solution consists of a saturated solution of silver nitrate in absolute alcohol (about 1-2%).

### 3. Alcoholic potassium hydroxide solution

Boil 0.5 ml of the compound with 4 ml alcoholic potassium hydroxide (0.5 N) under reflux for 15 minutes. Most alkyl halides give a crystalline precipitate of the potassium halide. Dilute with 5 ml of water, acidify with dilute nitric acid, and test with silver nitrate solution. The alcoholic potassium hydroxide solution (0.5 N) is prepared by dissolving 16 gm of potassium hydroxide pellets in 500 ml of alcohol (or industrial spirit) contained in a bottle closed by a cork. After standing for 24 hours, the clear solution is decanted or filtered from the residue of potassium carbonate. It is said that a solution in methyl alcohol has better keeping qualities than that in ethyl alcohol.

### Aliphatic aldehydes

Aliphatic aldehydes may be prepared by the controlled oxidation of primary alcohols with a solution of potassium or sodium dichromate in dilute sulphuric acid. To avoid the further oxidation to the corresponding acid, the aldehyde is removed as rapidly as possible by distillation through a fractionating column, for example:

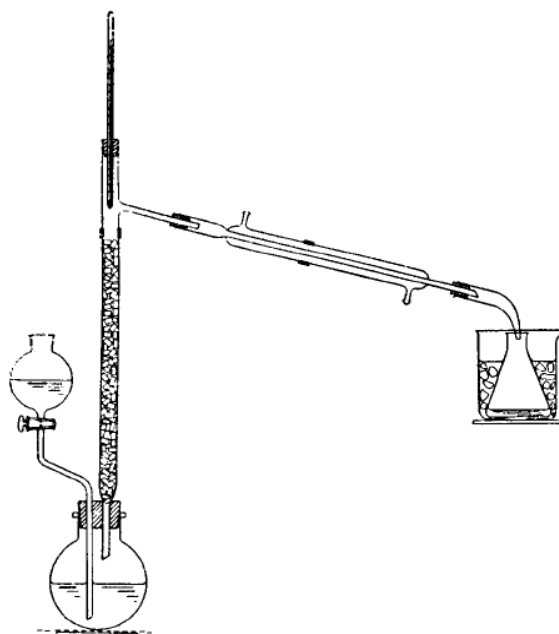


### Procedure of acetaldehyde preparation

Fit up the apparatus shown in Figure 9. The bolt-head flask is of 500 ml capacity and the Hempel column is filled with glass rings; the receiver is cooled in crushed ice or in cold water. Dissolve 56 gm of sodium dichromate dihydrate in 300 ml of water and add cautiously, with stirring, 40 ml of concentrated sulphuric acid. Place 51 ml of ethanol together with a few small chips of porous porcelain in the flask, and the acidified dichromate solution in the separatory funnel. Heat the ethanol to boiling so that the vapors



reach the lowest rings in the fractionating column. Run in the dichromate solution during about 15 minutes and at such a rate that the temperature at the top of the column does not rise above 80-85 °C. The oxidation to acetaldehyde proceeds with the evolution of heat, but it may be necessary to heat the mixture with a small flame from time to time in order to prevent the temperature from falling below 75 °C. When the entire oxidizing agent has been added, continue heating the mixture with a small flame for 15 minutes and collect all that passes over below 90 °C. Separate the small volume of water (*circa* 2 ml) from the distillate and dry the residue (29 gm) for 30-60 minutes with 3-4 gm of anhydrous magnesium sulphate. The yield is 13 gm pure acetaldehyde boils at 25° C.



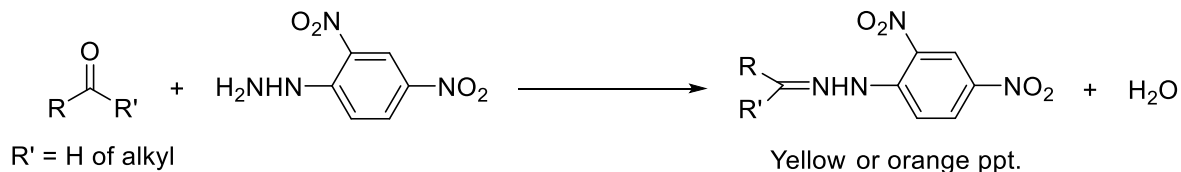
**Figure 9**

### **Reactions and characterization of aliphatic aldehydes**

The following reactions are characteristic of aliphatic aldehydes: those which are shared by ketones, due to the presence of the carbonyl group, are given under aliphatic ketones. Use the acetaldehyde for the following tests.

## 1. 2,4-Dinitrophenyl hydrazines

Both aldehydes and ketones contain the carbonyl group, hence a general test for carbonyl compounds will immediately characterize both classes of compounds. The preferred reagent is 2,4-dinitrophenylhydrazine which gives sparingly soluble phenyl hydrazones with carbonyl compounds:



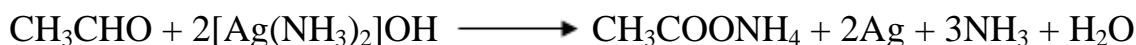
Reaction with 2,4-dinitrophenyl hydrazones, add 2 drops (or 0.05 gm) of substance to be tested to 3 ml of the 2,4-dinitrophenylhydrazones reagent, and shake if no precipitate forms immediately allow to stand for 5-10 minutes a crystalline precipitate indicates the presence of a carbonyl compound.

## Oxidation aldehyde by sodium dichromate in dilute sulphuric acid



## 1. Reaction of ammoniacal silver nitrate solution (Tollen's solution)

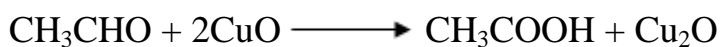
Add a few drops of a dilute solution of the aldehyde to 2-3 ml of an ammoniacal solution of silver nitrate [this contains the ion  $\text{Ag}(\text{NH}_3)_2^{+1}$ ] in a clean test-tube. A silver mirror is deposited on the walls of the tube either in the cold or upon warming in a beaker of boiling water.



## 2. Reduction of Fehling's solution

Place 4 ml of freshly prepared Fehling's solution (made by mixing equal volumes of Fehling's solution 1 (copper sulphate solution) and Fehling's solution 2 (alkaline tartrate

solution)] in a test-tube. Add 2-3 drops of acetaldehyde and boil the solution. A bright red precipitate of cuprous oxide is ultimately formed.



### Preparation of Fehling's solution:

**Solution No. 1.** Dissolve 34-64 gm of A.R. copper sulphate crystals in water containing a few drops of dilute sulphuric acid, and dilute the solution to 500 ml. **Solution No. 2.** Dissolve 60 gm of pure sodium hydroxide and 173 gm of pure Rochelle salt (sodium potassium tartrate) in water, filter if necessary through a sintered glass funnel, and make up the filtrate and washings to 500 ml. Keep the two solutions separately in tightly stoppered bottles and mix exactly equal volumes immediately before use.

**Note:** aliphatic aldehydes reduce Fehling solution immediately but aromatic aldehydes don't reduce it.

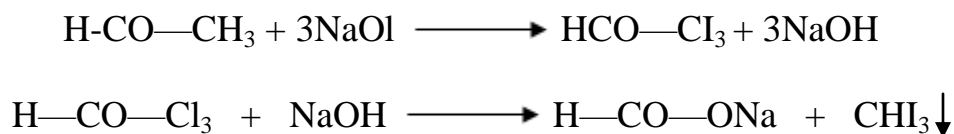
#### 1. Test with Schiff's reagent (Fuchsin aldehyde reagent).

Add 1 drop of acetaldehyde to 2-3 ml of water, and to this solution add 1 ml. of Schiff's reagent. Observe the production of a pink or bluish-red coloration

#### 2. Haloform test:

It is applicable to all compounds containing the  $\text{COCH}_3$  group (*e.g.*, acetaldehyde  $\text{RCOH}$  and  $\text{RCOCH}_3$ ) Acetone ( $\text{R} = \text{CH}_3$ ) when treated with sodium hypoiodite or bleaching powder solution yields iodoform.

To 1ml. of acetaldehyde add 3 ml from iodine solution in potassium iodide (10%) then added drop by drop solution  $\text{NaOH}$  (10%) until the iodine color disappear and the solution became yellow then precipitate of iodoform is formed



## Reactions and characterization of aliphatic ketones

Ketones, unlike aldehydes do not (a) reduce ammoniacal solutions of silver salts, (b) reduce Fehling's solution, (c) react with Schiff's reagent, (d) yield resins with strong sodium hydroxide solution. Most ketones contain the  $\text{COCH}_3$  grouping (*e.g.*, acetone) {excluding those possessing the phenyl  $\text{C}_6\text{H}_5$  grouping} or those which contain the  $\text{RCOR}$  grouping as part of the ring (*e.g.*, cyclohexanone).

Most of the characteristic reactions of ketones ( $\text{RR}'\text{CO}$ ) depend upon condensation with substituted amines. The reactions occur between the carbonyl group and the  $\text{NH}_2$  group of the substituted amine, and hence are also shared by aldehydes  $\text{RCHO}$ :

### 1. Hydrazine ( $\text{NH}_2\text{NH}_2$ )

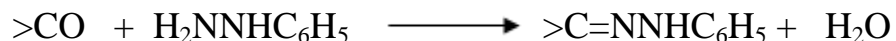
The product formed is called a hydrazine, but since this derivative possesses a free amino group it can condense with another molecule of the carbonyl compound to yield hydrazine:



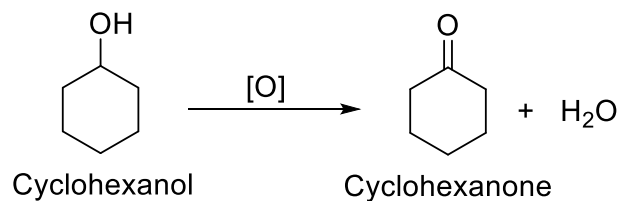
This double condensation is prevented by the use of substituted hydrazine

### 2. Phenylhydrazine ( $\text{C}_6\text{H}_5\text{NHNH}_2$ )

Carbonyl compounds react with phenyl hydrazine to give phenyl hydrazones. These derivatives are largely oils (or possess low melting points) for many aliphatic aldehydes and ketones, but are generally crystalline for aromatic carbonyl compounds and also for cycloaliphatic and heterocyclic aldehydes and ketones,



Aliphatic ketones may be prepared by the oxidation of secondary alcohols with potassium dichromate and dilute sulphuric acid, for example:



## Cyclohexanone

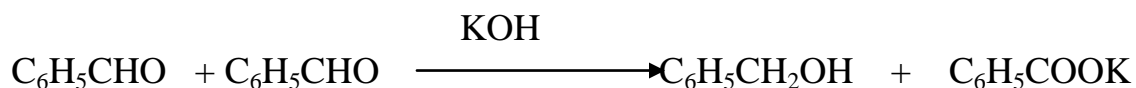
Dissolve 2.5 gm of sodium dichromate dihydrate in 12.5 ml of water in a 600 ml beaker and add carefully, with continuous stirring, 44 gm (24 ml) of concentrated sulphuric acid. Allow the mixture to cool. Place 13 ml of cyclohexanol: in a 500 ml conical or flat-bottomed flask, and add the dichromate solution to it in one portion. Shake the mixture to ensure thorough mixing and observe the temperature with a thermometer. Considerable heat is evolved in the oxidation. When the temperature rises to 55 °C, cool the flask in a vessel of cold water or under the tap; sufficient external cooling should be applied to keep the temperature between 55 °C and 60 °C, *i.e.*, the temperature must not be allowed to fall below 55 °C or rise above 60 °C. When the temperature of the mixture no longer rises above 60 °C upon the removal of the external cooling, allow the flask to stand with occasional shaking for 1 hour.

Pour the reaction mixture into a 1-litre round-bottomed flask, add 30 ml of water, and fit a still head and a condenser for downward distillation but without the thermometer). Distil the mixture until about 125 ml of distillate (two layers) have been collected. Saturate with salt (about 30 gm are required), and separate the upper layer of cyclohexanone: extract the aqueous layer with 25-30 ml of ether and combine the ether extract with the cyclohexanone layer. Dry with about 0.6 gm of anhydrous sodium or magnesium sulphate; filter the solution into a distilling flask of suitable size to which a condenser has previously been attached. Distil off the ether from a water bath; a beaker containing warm water is satisfactory. Distil the residual liquid from air bath or ware gauze, and collect the cyclohexanone at 153-156 °C.

## Condensation reactions of aromatic aldehydes

### Cannizzaro reaction

Aromatic aldehydes (and other aldehydes in which  $\alpha$ -hydrogen atoms are absent, *e.g.*, formaldehyde, trimethylacetaldehyde, and hydroxy-*iso*-butyraldehyde) under the influence of strong aqueous or alcoholic alkali undergo simultaneous oxidation and reduction yielding the alcohol and corresponding acid, thus:

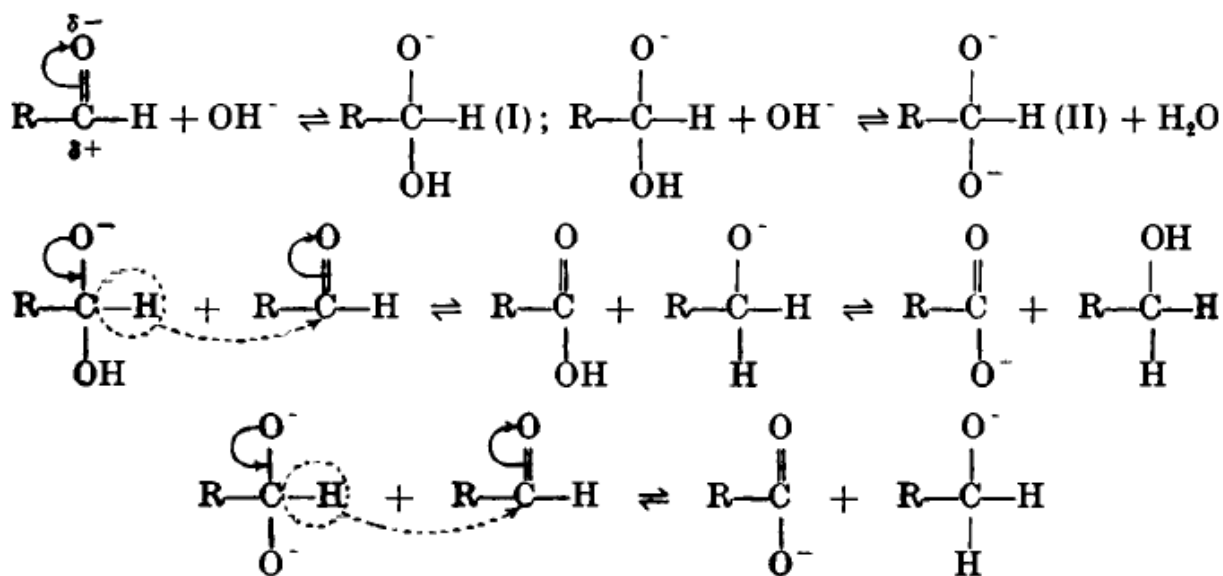


Benzaldehyde

Benzyl alcohol

Potassium benzoate

The mechanism of the reaction probably involves the production, by interaction of the aldehyde with hydroxide ions, of two reducing anions, the first (I) more easily than the second (II). Either of these anions may transfer a hydride ion to a carbonyl carbon atom in another aldehyde molecule:



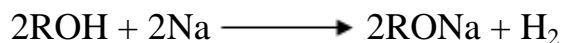
### **Procedure (Cannizzaro Reaction)**

Dissolve 27 gm of potassium hydroxide in 25 ml of water contained in a beaker or conical flask, and cool the solution to about 20 °C in ice water. Pour the solution into a 250 ml reagent bottle, and add 30 gm (29 ml) of pure benzaldehyde (1); *cork* the bottle securely and shake the mixture vigorously until it has been converted into a thick emulsion. Allow the mixture to stand overnight or for 24 hours in the stoppered bottle. Add just sufficient water (about 105 ml) to dissolve the potassium benzoate. Pour the liquid into a separatory funnel, rinse out the bottle with about 30 ml of ether and add this ether to the solution in the funnel. Shake the solution in order to thoroughly extract the benzyl alcohol with the ether, separate the lower aqueous solution, and carry out two further extractions each with about 25 ml of ether (Save the aqueous solution). Combine the ether extracts. Cool and shake the ether solution twice with 5 ml portions of saturated sodium bisulphite solution in order to remove any benzaldehyde which may be present. Separate the ethereal solution, wash it with 10 ml of 10% sodium carbonate solution (to ensure complete removal of the bisulphite), then with 10 ml of water, and dry with anhydrous magnesium sulphate or anhydrous potassium carbonate. Remove the ether on a water bath, (the pure compound boils at 205.5 °C), the yield is 13 gm. Pour the aqueous solution remaining from the ether extraction with stirring into a mixture of 80 ml of concentrated hydrochloric acid, 80 ml of water and about 100 gm of crushed ice. Filter the precipitated benzoic acid at the pump,

wash it with a little cold water, drain, and recrystallize from boiling water. The yield of benzoic acid (colorless crystals), m.p. 121 °C, is 18 gm.

### Reactions and characterization of aliphatic alcoholic

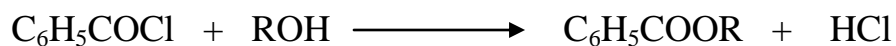
1. Metallic sodium reacts with alcohols with the evolution of hydrogen:



Methanol > 1° > 2° > 3° the reactivity of alcohols toward metallic sodium

Treat 2 ml. of absolute methyl alcohol with a small of dry, freshly-cut sodium. Observe the result. Cool the solution when *all* the sodium has reacted. Add a little water and test the solution with litmus paper. Obtain five small dry test-tubes (75 X 10 mm) and introduce 1 ml. of the following alcohols into each: ethyl alcohol, *n*-butyl alcohol, *sec.*-butyl alcohol, and cyclohexanol and *tert*-butyl alcohol. Add a minute fragment of sodium to each and observe the rate of reaction. Arrange the alcohols in the order of decreasing reactivity towards sodium. Traces of water, present as impurities, would give an initial evolution of hydrogen, but reaction would stop after a time if an alcohol is absent: furthermore, certain esters and ketones also evolve hydrogen when treated with sodium. It may, however, be assumed that if no hydrogen is evolved in the test, the substance is not an alcohol.

2. Reaction with acetyl chloride reacts vigorously with primary and secondary alcohols to yield esters; it also reacts readily with any water present to form acetic acid: The resulting esters differ sufficiently in odor and water solubility to be readily distinguished from the original alcohol.





Treat 1 ml. of the alcohols enumerated in (1) cautiously with 0.5-0.7 ml of acetyl chloride. Observe the reaction which occurs. After 2-3 minutes, pour the contents of the various test-tubes into 3 ml portions of water, neutralize the aqueous layer with solid sodium bicarbonate, and examine the residual liquids for odor and density (relative to water).

### 3. Differentiation between primary, secondary, and tertiary alcohols (Lucas test)

The test depends upon the different rates of formation of the alkyl chlorides upon treatment with a hydrochloric acid / zinc chloride reagent (containing 1 mole of acid to 1 mole of anhydrous zinc chloride) and with hydrochloric acid. It applies only to aliphatic and cycloaliphatic alcohols. To 1 ml of the alcohol in a small test-tube, add quickly 6 ml of Lucas' reagent at 26-27 °C, close the tube with a cork, shake, and allow to stand. Observe the mixture during 6 minutes. The following results may be obtained:

(a) Primary alcohols lower than hexyl, dissolve; there may be some darkening, but the solution remains clear.

(b) Primary alcohols, hexyl and higher, do not dissolve appreciably; the aqueous phase remains clear.

(c) Secondary alcohols: the clear solution becomes cloudy owing to the separation of finely-divided drops of the chloride

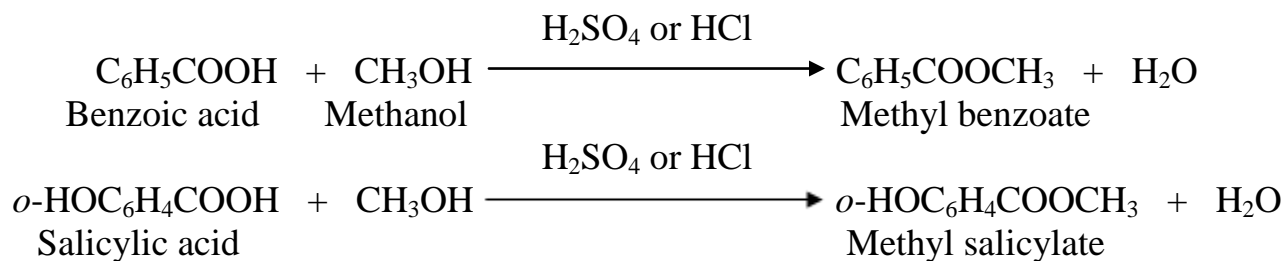
A distinct upper layer is visible after one hour except for *iso*-propyl alcohol (probably because of the volatility of the chloride).

(d) Tertiary alcohols: two phases separate *almost immediately* owing to the formation of the tertiary chloride. If a turbid solution is obtained, it will be suggesting the presence of a secondary alcohol but not excluding a tertiary alcohol.

### Aromatic esters

Aromatic esters may be prepared by methods similar to aliphatic esters. From the acid. By refluxing an aromatic acid (1 mol) with an excess (up to about 10 moles) of methyl or ethyl alcohol in the presence of a small proportion of concentrated sulphuric acid or hydrogen chloride (catalyst), the ester may be obtained in good yield. The excess of methyl or ethyl

alcohol may be largely removed by distillation from a water bath or, less conveniently, by pouring into a large excess of water. For higher alcohols, *e.g.*, *n*-propyl or *n*-butyl alcohols, the proportion of alcohol may be considerably reduced (say, 1 mol of monobasic acid to 2 moles of alcohol) if a volume of pure dry benzene approximately equal to that of the alcohol is added. The following examples are given:



## Methyl benzoate

### Procedure

In a 500 ml. round-bottomed flask place a mixture of 30 g. of benzoic acid, 80 gm (101 ml) of absolute methyl alcohol and 6 gm (2-7 ml) of concentrated sulphuric acid. Add a few small chips of porous porcelain attach a reflux condenser and boil the mixture gently for 4 hours (1). Distil off the excess of alcohol on a water bath and allow cooling. Pour the residue into about 250 ml of water contained in a separatory funnel and rinse the flask with a few ml. of water which are also poured into the separatory funnel. If, owing to the comparatively slight difference between the density of the ester and of water, difficulty is experienced in obtaining a sharp separation of the lower ester layer and water, add 10-15 ml of carbon tetrachloride (2) and shake the mixture in the funnel vigorously; upon standing, the heavy solution of methyl benzoate in the carbon tetrachloride separates sharply and rapidly at the bottom of the separatory funnel. Run off the lower layer carefully, reject the upper aqueous layer, return the methyl benzoate to the funnel and shake it with a strong solution of sodium bicarbonate until all free acid is removed and no further evolution of carbon dioxide occurs. Wash once with water, and dry by pouring into

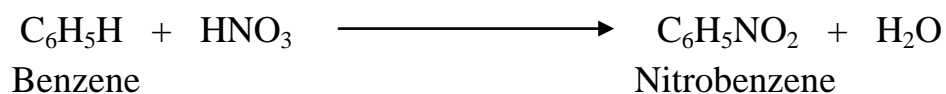
a small dry conical flask containing about 5 gm of anhydrous magnesium sulphate. Cork the flask, shake for about 5 minutes, and allow standing for at least half an hour with occasional shaking. Filter the methyl benzoate solution through a small fluted filter paper directly into a small distilling flask containing a few chips of unglazed porcelain (porous pot). Fit the flask with a 360 °C thermometer and a condenser (a simple air condenser may be used, but a small Liebig's condenser with an empty water jacket is quite satisfactory). Distil from an air bath; raise the temperature slowly at first (3) until all carbon tetrachloride has passed over and then heat more strongly. Collect the methyl benzoate (a colorless liquid) at 198-200 °C, yields is 31 gm.

**Notes:**

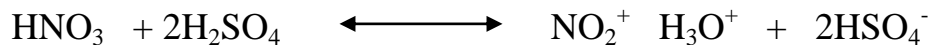
1. Slightly improved results may be obtained by increasing the time of heating.
2. Alternatively, the ester may be extracted with two 50 ml portions of ether. The ethereal solution is washed with concentrated sodium bicarbonate solution (handle the separatory funnel cautiously as carbon dioxide is evolved) until effervescence ceases, then with water, and dried over anhydrous magnesium sulphate. The ether is removed with the aid of the apparatus, and the residual ester distilled.
3. In view of the small quantity of carbon tetrachloride present, the use of water condenser during the early stages of the distillation, although desirable for complete recovery of the solvent, is not essential.

**Nitration of aromatic hydrocarbons**

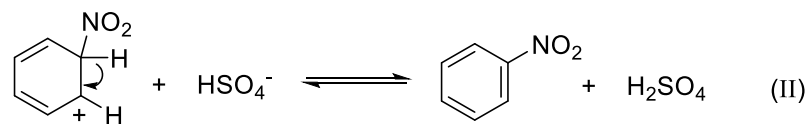
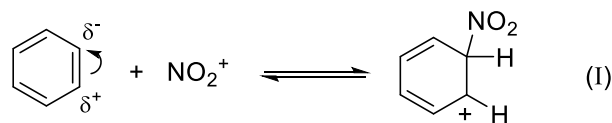
Aromatic hydrocarbons may be nitrated, i.e., the hydrogen atoms replaced by nitro (NO<sub>2</sub>) groups, with concentrated nitric acid in the presence of concentrated sulphuric acid, for example :



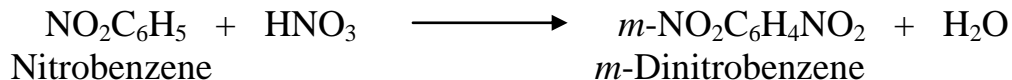
The function of the sulphuric acid is to furnish a strongly acid medium and to convert the nitric acid into the highly reactive nitronium ion  $\text{NO}_2^+$ , which is the real nitrating agent:



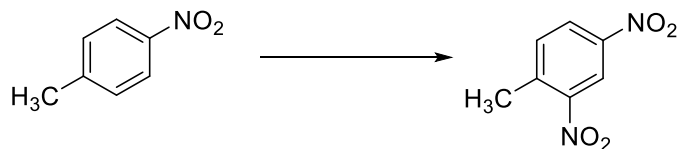
The mechanism of the aromatic substitution may involve the attack of the electrophilic  $\text{NO}_2$  ion upon the nucleophilic aromatic nucleus to produce the carbonium ion (I); the latter transfers a proton to the bisulphate ion, the most basic substance in the reaction mixture



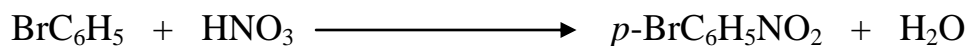
Nitration reaction is usually carried out at comparatively low temperatures; at higher temperatures there may be loss of material because of the oxidizing action of the nitric acid. For substances which do not nitrate readily with a mixture of concentrated nitric and sulphuric acids (mixed acid), the intensity of the reaction may be increased *inter alia* by the use of fuming sulphuric acid (containing up to 60% of sulphur trioxide) or by fuming nitric acid. Thus nitrobenzene is converted by a mixture of fuming nitric acid and concentrated sulphuric acid into about 90%, of *m*-dinitrobenzene and small amounts of the *o*- and *p*-isomers; the latter are eliminated in the process of recrystallization:



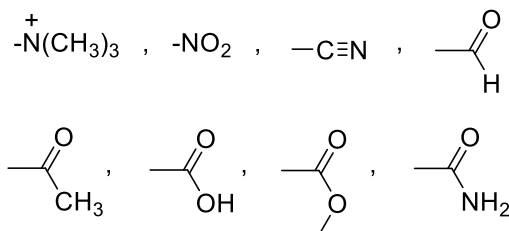
*p*-Nitrotoluene is similarly converted largely into 2,4-dinitrotoluene:



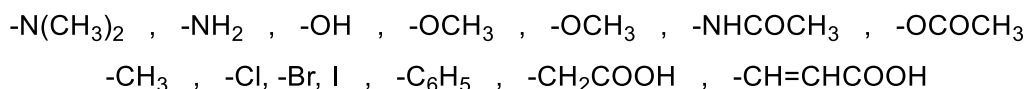
Nitration of bromobenzene with "mixed acid" yields largely *p*-bromonitrobenzene accompanied by a little of the *o*-isomeride:



A brief account of aromatic substitution may be usefully given here as it will assist the student in predicting the orientation of disubstituted benzene derivatives produced in the different substitution reactions. For the nitration of nitrobenzene, the substance must be heated with a mixture of fuming nitric acid and concentrated sulphuric acid: the product is largely *m*-dinitrobenzene (about 90%), accompanied by a little *o*-dinitrobenzene (about 5%) which is eliminated in the recrystallization process. On the other hand phenol can be easily nitrated with dilute nitric acid to yield a mixture of *ortho* and *para* nitrophenols. It may be said, therefore, that orientation is *meta* with the nitro group and *ortho* - *para* with the hydroxyl group. The nitro group (NO<sub>2</sub>) is unsaturated and possesses a positively charged atom in the key position adjacent to the benzene ring, whereas the hydroxyl group is fully saturated. The *meta*-directing nitro group renders substitution more difficult, *i.e.*, exerts a deactivating effect on the aromatic nucleus: the *ortho* - *para* directing hydroxyl group, however, facilitates substitution, *i.e.*, exerts an activating influence on the aromatic nucleus. Most other substituent groups are sufficiently similar to the types exemplified by the nitro group or the hydroxyl group to justify an empirical classification into *meta* and *ortho* - *para* directing groups. The *meta* directing groups include those in which the atom directly attached to the aromatic nucleus is either positively charged or strongly unsaturated. These are, in order of decreasing effectiveness:



The *ortho* -*para* directing groups include those which are saturated or only weakly unsaturated at the point of the attachment of the ring. These are



### ***m*-Dinitrobenzene**

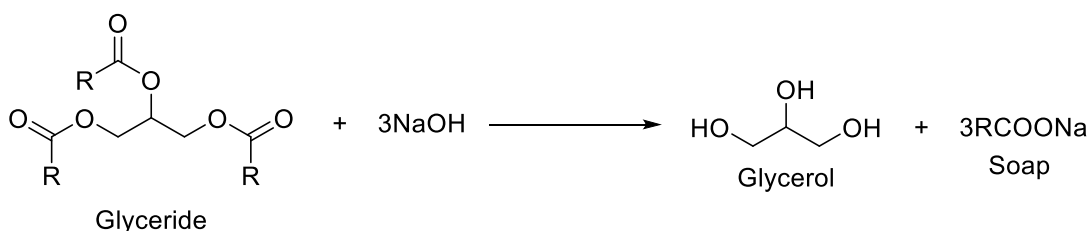
#### **Procedure:**

Place 37.5 gm(21 ml) of concentrated sulphuric acid and 15 ml of fuming nitric acid, sp. gr. 1-5, in a 250 or 500 ml round-bottomed flask; add a few fragments of unglazed porcelain or of broken glass.

Attach a reflux condenser and place the apparatus in a fume chamber. Add slowly, in portions of about 12-5 ml of nitrobenzene; after each addition, shake the flask to ensure thorough mixing. Heat the mixture, with frequent shaking, on a boiling water bath; securely clamp both the flask and condenser since the acid fumes usually attack the cork. Allow the mixture to cool somewhat and pour it cautiously with vigorous stirring into about 500 ml. of cold water; the dinitrobenzene soon solidifies. Filter with suction, wash thoroughly with cold water, and allow draining as completely as possible. Transfer the crude dinitrobenzene to a 250 ml flask fitted with a reflux condenser, add 80-100 ml of methylated (or rectified) spirit and heat on a water bath until all the crystalline solid dissolves. If the resulting solution is not quite clear, filter it through a fluted filter paper on a large funnel which has previously been warmed or through a warm Buchner funnel. Colorless crystals of *m*-dinitrobenzene (15 gm) are deposited on cooling. If the m.p. is below 89-90 °C, recrystallization is necessary.

## Soaps

The term fat is applied to solid esters of fatty acids with glycerol (glycerides); if the fat is liquid at the ordinary temperature, it is conventionally called a fatty oil, vegetable oil or animal oil. The acids which occur most abundantly are palmitic acid  $\text{CH}_3(\text{CH}_2)_{14}\text{COOH}$ , stearic acid  $\text{CH}_3(\text{CH}_2)_{16}\text{COOH}$  and oleic acid  $\text{CH}_3(\text{CH}_2)_7\text{CH}=\text{CH}(\text{CH}_2)_7\text{COOH}$ . Upon hydrolysis, fats yield glycerol and the alkali salts of these acids (soaps):



### Saponification of fat (Soap) (Detergents)

Place 5 gm of lard (or any fat or fatty oil), 3 gm of potassium hydroxide and 40 ml. of alcohol in a 250 ml round-bottomed flask, attach a reflux condenser, and boil for about 30 minutes. The reaction is complete when no globules of oil are present when a few drops of the mixture are mixed with a little water. Distil the reaction mixture and recover the alcohol; dissolve the residue in 75 ml of hot water. Carry out the following experiments with the resulting solution:

1. To 25 ml of the solution adds slowly and with stirring a saturated solution of sodium chloride. Filter off the precipitate of soap and wash it with a little saturated sodium chloride solution, and spread it on a watch glass to dry. Test a portion of the product for its lathering properties by rubbing it with water between the hands. Use another portion to determine whether it is soluble in water.
2. Mix 10 ml of the solution with an equal volume of tap water, shake well and observe the result.