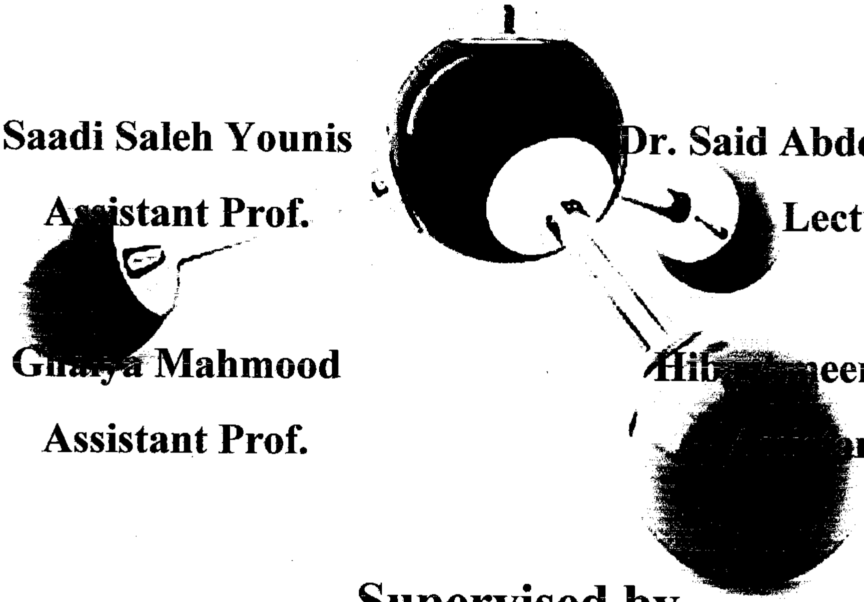
University of Mosul
College of Science
Dept. of Chemistry

A BOOKLET OF PRACTICTAL ORGANIC CHEMISTRY

FOR

THIRD YEAR STUDENTS

Prepared by



Saadi Saleh Younis
Assistant Prof.

Dr. Said Abdel-Qader Said
Lecturer

Ghaiya Mahmood
Assistant Prof.

Hib[illegible]een Ibraheem
Assistant Lect.

Supervised by

Dr. Said Abdel-Qader Said

INTRODUCTION

Since many aspects of development and knowledge in the field of chemistry require to study in English , we have found that it is essential to prepare this booklet in the field of Practical Organic Chemistry in English , to become a scientific foundation for chemistry students in the College of Science .

The experiments are thoughtfully selected to introduce you to the common laboratory practices and techniques of organic chemistry and to illustrate the chemistry of the wide range of functional groups that are present in organic molecules . These experiments are designed to allow you to synthesize specific compounds which are of commercial importance using reactions that are fundamental to organic synthesis .

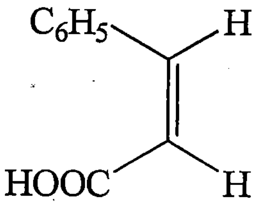
CONTENTS

Perkin reaction

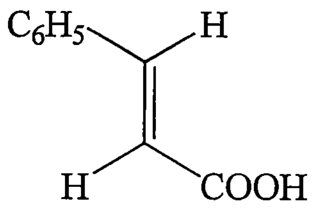
(Synthesis of Cinnamic acid)

Theory : The condensation of an aromatic aldehyde with an acid anhydride in the presence of sodium or potassium salt of the acid corresponding to the anhydride to yield α , β – unsaturated acid is known as the Perkin reaction . Thus benzaldehyde when heated with a mixture of acetic anhydride and sodium acetate gives rise to cinnamic acid . Theoretically , cinnamic acid can be present in two possible forms (cis and trans) , the Perkin reaction gives rise only to the trans form (m.p. 133°C) .

The cis form of cinnamic acid (termed *allo* - cinnamic acid) is unstable and easily converted into the trans form .

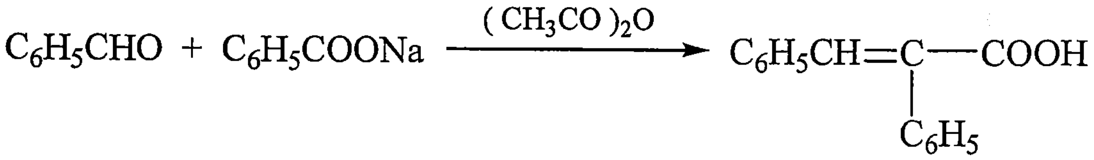


Allo - cinnamic acid
(cis)



Cinnamic acid
(trans)

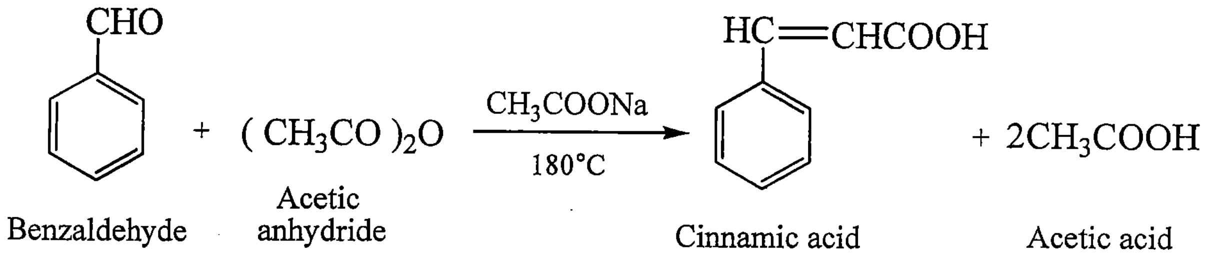
It is worth mentioning that the use of an alkali salt of a carboxylic acid differ from the anhydride used , it will produce the substituted cinnamic acid :



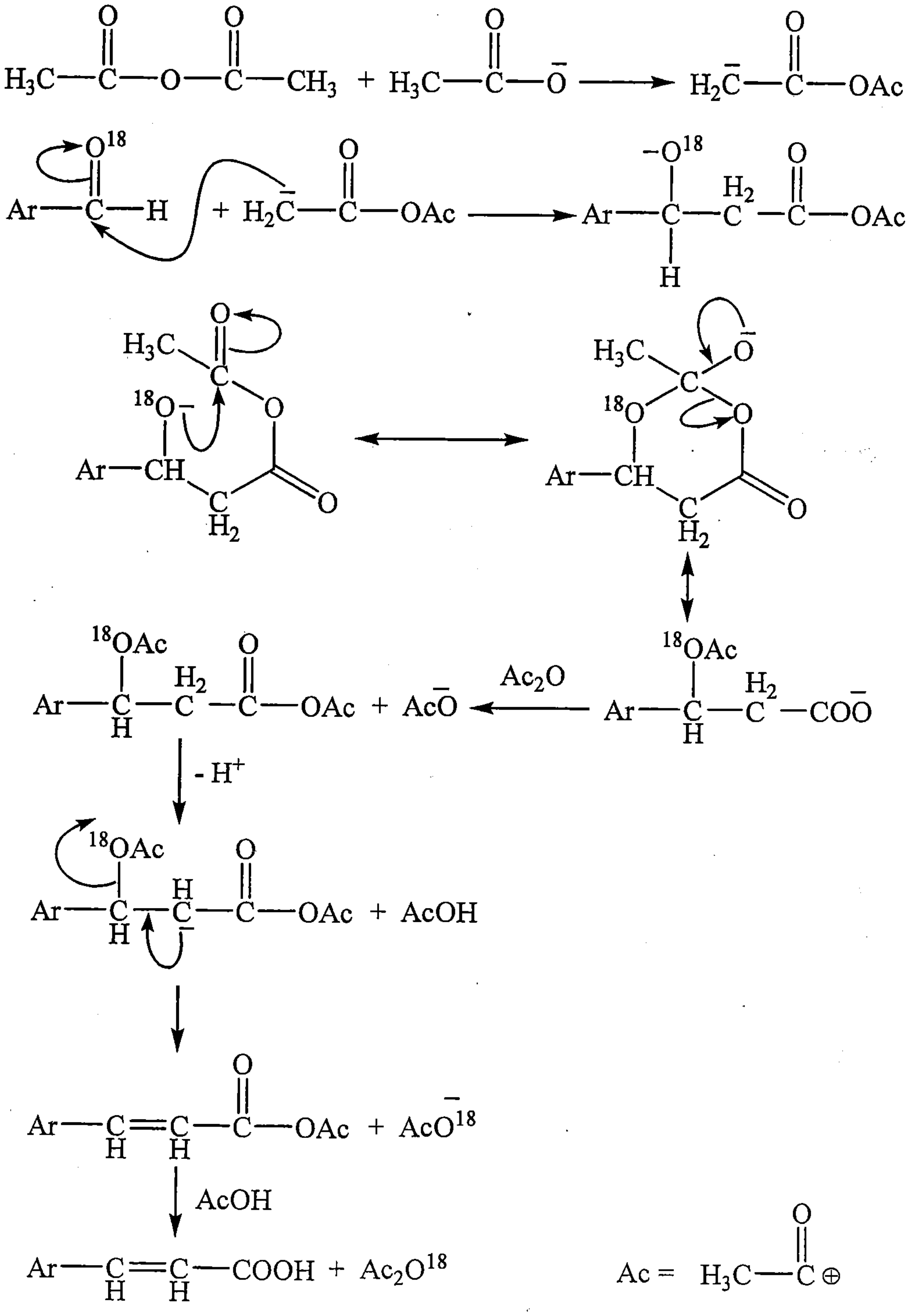
$$C_6H_5CHO + C_6H_5COONa \xrightarrow{(CH_3CO)_2O} C_6H_5CH{=}\underset{\displaystyle C_6H_5}{\underset{|}{C}}{-}COOH$$

(α - Phenyl cinnamic acid)

General equation :



Mechanism :



Theoretical calculations table :

Reactants	Products	Vol.	Density	Wt.	M.wt.	n	m.p.	b.p.
Benzaldehyde	---	5 mL	1.04	5.2	106	0.049	- 26	179
Acetic anhydride	---	7 mL	1.08	7.56	102	0.074	-73	140
---	Cinnamic acid							

Calculation of percentage yield of the product :

$$\% = \frac{\text{no. of moles of the product}}{\text{no. of moles of the reactant}} \text{ X } 100$$

Procedure :

Note : All equipments must be clean and dry .

1st. week

1) In a (100 mL) round bottomed flask fitted with an air condenser , place (5 mL) of benzaldehyde , (7mL) of acetic anhydride and (3g.) of sodium acetate .

2) Heat the reaction mixture in a sand bath (Fig. 1) at (170 – 180° C) for at least (2 hours) .

3) Cool the mixture , then pour it into (75 mL) of water contained in a (250 mL) conical flask , then turn the acidic medium to basic medium by treating the solution with sodium carbonate until the red colour of litmus paper turns to blue .

2nd. week

4) Steam distil the solution (Fig. 2) until all the unchanged benzaldehyde removed and the distillate is clear .

5) Cool the residual solution and filter at the pump to remove unsoluble materials .

6) Acidify the filtrate by adding diluted hydrochloric acid to precipitate cinnamic acid from its salt .

7) Filter the cinnamic acid at the pump and wash with cold water .

3rd. week

8) Recrystallise the product from water to get pure cinnamic acid .

9) Determination of melting point of the product will be made after drying , then weigh the product and calculate the percentage yield .

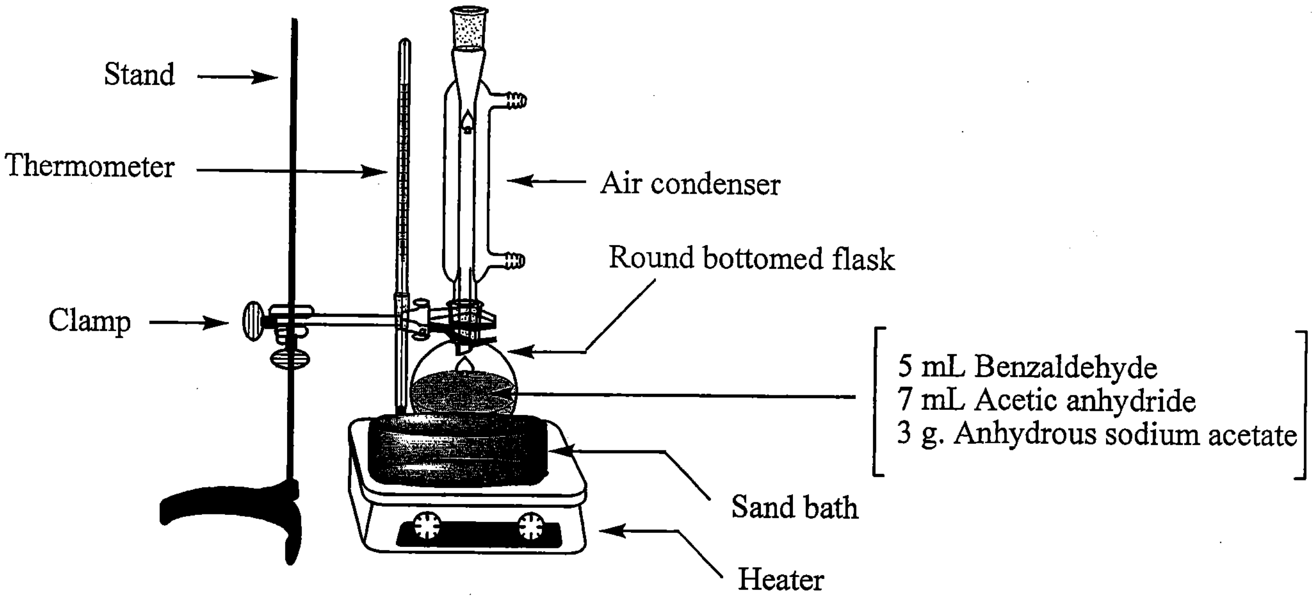

Stand
Thermometer
Air condenser
Round bottomed flask
Clamp
5 mL Benzaldehyde
7 mL Acetic anhydride
3 g. Anhydrous sodium acetate
Sand bath
Heater

Fig. (1)

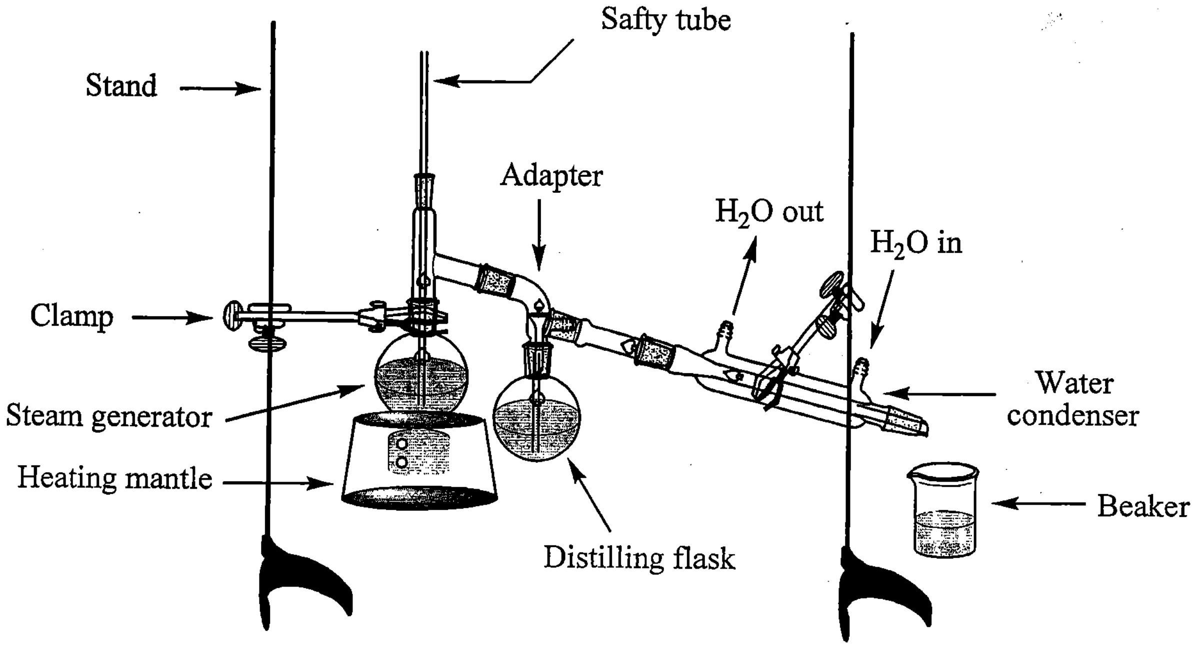

Safty tube
Stand
Adapter
H2O out
H2O in
Clamp
Steam generator
Water condenser
Heating mantle
Beaker
Distilling flask

Fig. (2)

Cannizzaro Reaction

(Benzyl alcohol and benzoic acid)

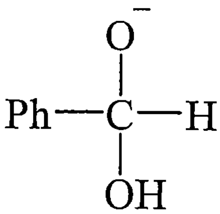
Theory : Aromatic aldehydes like benzaldehyde (and other aldehydes in which α–hydrogen atoms are absent , e.g. , formaldehyde and trimethylacetaldehyde) under the influence of strong alkali undergo simultaneous oxidation and reduction yielding the alcohol and the corresponding acid . This reaction is known as Cannizzaro reaction as shown in the following equation :

$$2\,PhCHO + NaOH \longrightarrow PhCH_2OH + PhCOOH$$

On the other hand the reaction that involve the reduction of an aldehyde by formaldehyde giving the corresponding alcohol is known as (crossed Cannizzaro reaction) as shown below :

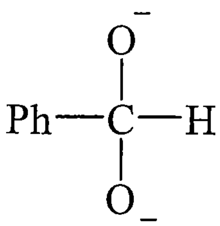
$$\begin{tikzcd}
PhCHO + HCHO \arrow[r, "KOH"] & PhCH_2OH + HCOOK \arrow[d, "HCl"] \\
 & HCOOH
\end{tikzcd}$$

The mechanism of this reaction involves the formation of tow reducing anions through the reaction of the benzaldehyde with the hydroxide ion . The formation of anion (I) is more easier than anion (II) . Either of these anions may transfer a hydride ion (H^-) to a carbonyl atom in another aldehyde molecule .



$$Ph-\underset{OH}{\overset{O^-}{C}}-H$$

(I)



$$Ph-\underset{O^-}{\overset{O^-}{C}}-H$$

(II)

General equation :

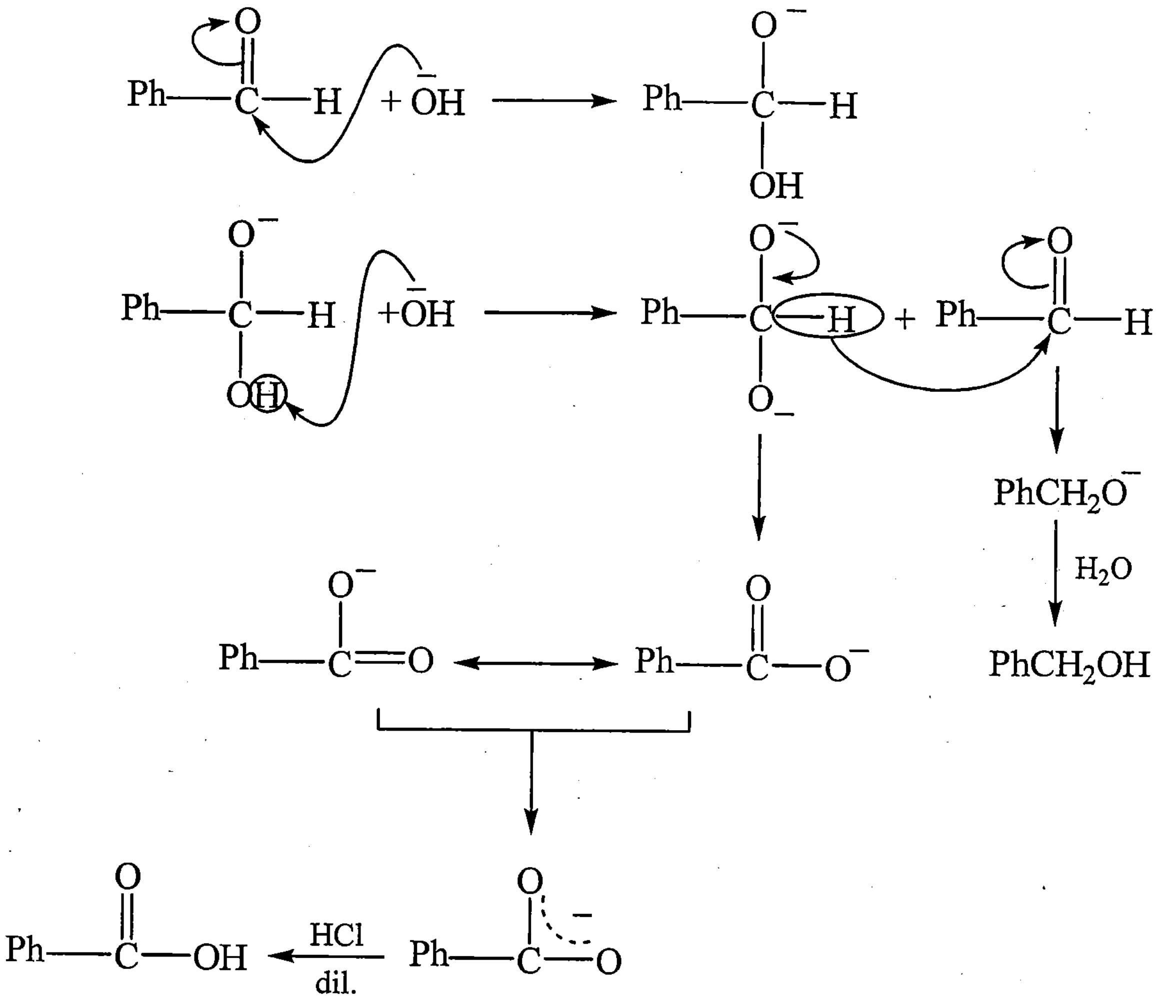
$$2\,PhCHO \xrightarrow[\text{conc.}]{NaOH} PhCH_2OH + PhCOOH$$

Benzaldehyde

Benzyl alcohol

Carboxylic acid
Benzoic acid

Mechanism :



Theoretical calculations table :

0.0036

Reactants	Products	Vol.	Density	Wt.	M.wt.	n	m.p.	b.p.
benzaldehyde	---	7.5 mL	1.04	7.8	106	0.073	- 26	179
---	Benzyl alcohol							
---	Benzoic acid							

Calculation of percentage yield of the product :

$$\% = \frac{\text{no. of moles of the product}}{\text{no. of moles of the reactant}} \text{ X } 100$$

Procedure :

1) Dissolve (7 g.) of sodium hydroxide in a (7 mL) of water contained in a (100 mL) flat bottomed flask as shown in fig. (3) .

2) Add (7.5 mL) of pure benzaldehyde ; then cork the flask securely and shake the mixture until it has been converted into thick emulsion .

3) Allow the mixture to stand overnight in the stoppered flask .

1st. week

The mixture in the flask is consist of the following compounds :

a) Sodium benzoate

b) Benzyl alcohol

c) Unreacted benzaldehyde

1) Dissolve the sodium benzoate in a sufficient amount of water (50–60 mL) by shaking .

2) Pour the solution into a separatory funnel as shown in fig. (4) , rinse out the flask with about (15 mL) of ether and add this ether to the solution in the funnel .

3) Shake the solution in order to thoroughly extract the benzyl alcohol and the unreacted benzaldehyde .

4) Separate the aqueous layer in a (250 mL) conical flask .

5) Acidify the aqueous layer by adding diluted hydrochloric acid (with cooling and stirring) in order to precipitate benzoic acid from its salt .

6) Filter the precipitated benzoic acid at the pump , wash it with a little amount of cold water and leave the solid to the next week in order to purify it .

7) Shake the ether layer with a (10 mL) of saturated solution of sodium bisulphite in order to remove the unreacted benzaldehyde which may be present .

8) Separate the aqueous layer and wash the ethereal layer with (10 mL) of saturated solution of sodium bicarbonate to ensure complete removal of the bisulfite .

9) Remove the aqueous layer and wash the ethereal layer with (10 mL) of water .

10) Remove the water then place the ether layer in a (25 mL) conical flask and dry with anhydrous magnesium sulphate .

11) Filter the ether in dry (25 mL) conical flask and remove the ether (by evaporation) on a water bath then weigh the residual liquid (benzyl alcohol) and calculate the percentage yield .

2$^{nd.}$ week

12) Recrystallise the benzoic acid from boiling water .

13) Determination of melting point will be made after drying .

14) Weigh the product and calculate the percentage yield .

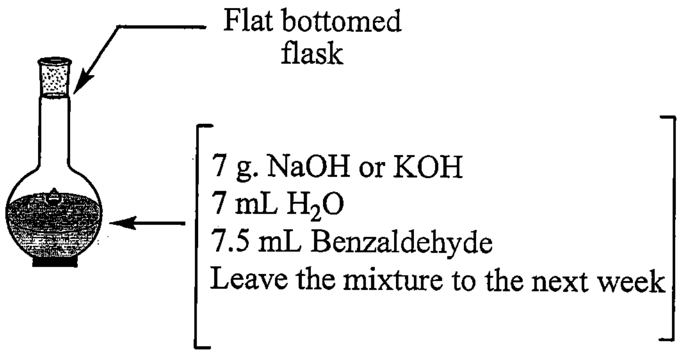

Flat bottomed flask
7 g. NaOH or KOH
7 mL H_2O
7.5 mL Benzaldehyde
Leave the mixture to the next week

Fig. (3)

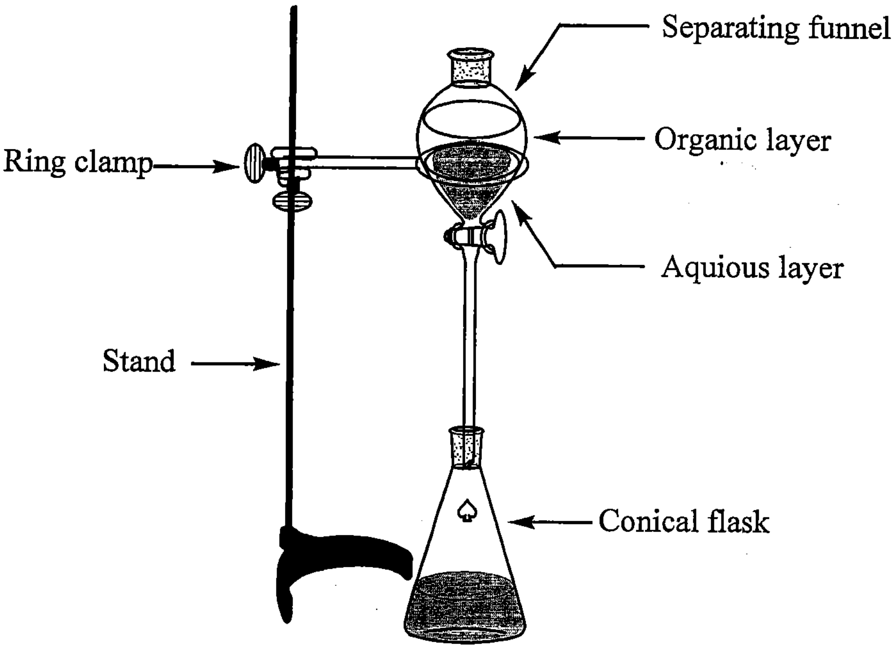

Separating funnel
Organic layer
Ring clamp
Aquious layer
Stand
Conical flask

Fig. (4)

Synthesis of Diazonium Salts

(Azo dye and phenol)

Theory : Amines undergoes different types of reactions , but their reaction with nitrous acid is the most important and useful one . These reactions involve the formation of different products which depend on amine kind (aromatic or aliphatic) , whether it is primary , secondary or tertiary .

The most important reaction is that involve the reaction of primary aromatic amine with nitrous acid below 0°C to afford relatively stable diazonium salt , since rising the temperature over 0°C will convert this salt to the corresponding phenol .

On the other hand diazonium salts of primary aliphatic amine are unstable and decompose directly after their formation to give alcohol or olefin and/or alkyl halide .

The process that involves the formation of diazonium salt is called (Diazotization) which can be represented in the following equation:

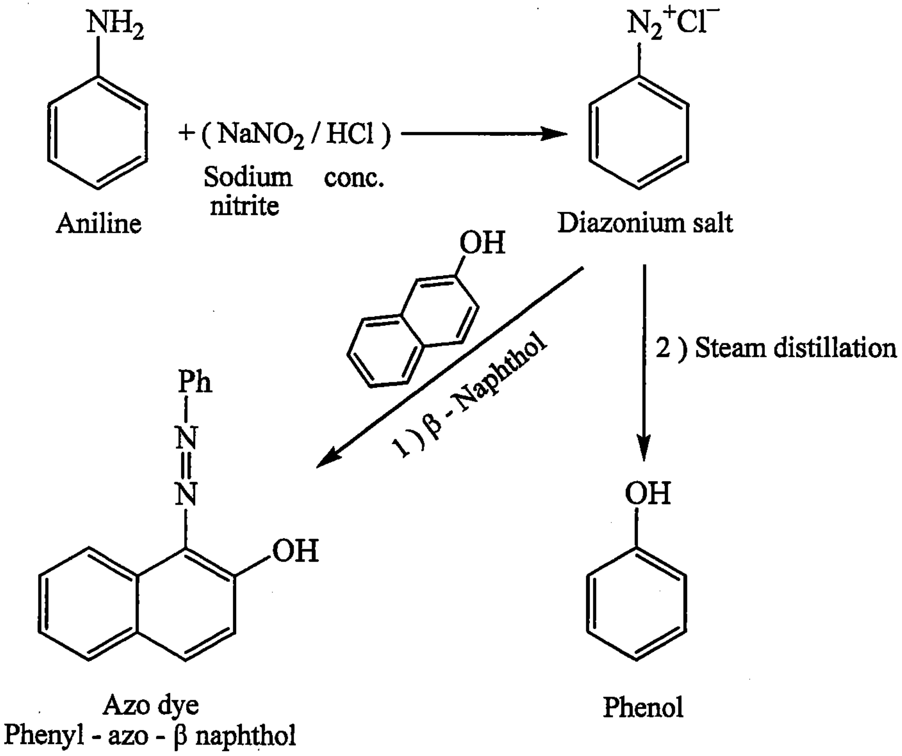
$$Ar{-}NH_2 + HONO \longrightarrow (Ar{-}N_2)^+ A^- + 2H_2O$$

The first step of this reaction involve nucleophilic attack of amine at nitrous acid.

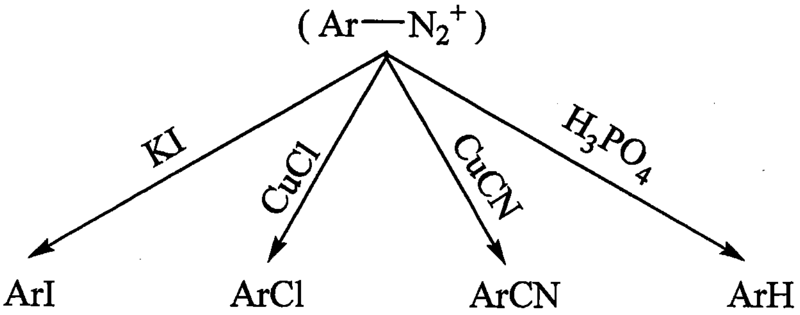
* The ease of the formation of diazonium salts depend on substituents properties and on the nature of the anion .

* Diazonium salts undergoes different types of reactions but the most important one is the formation azo dyes and phenols .

General equation :

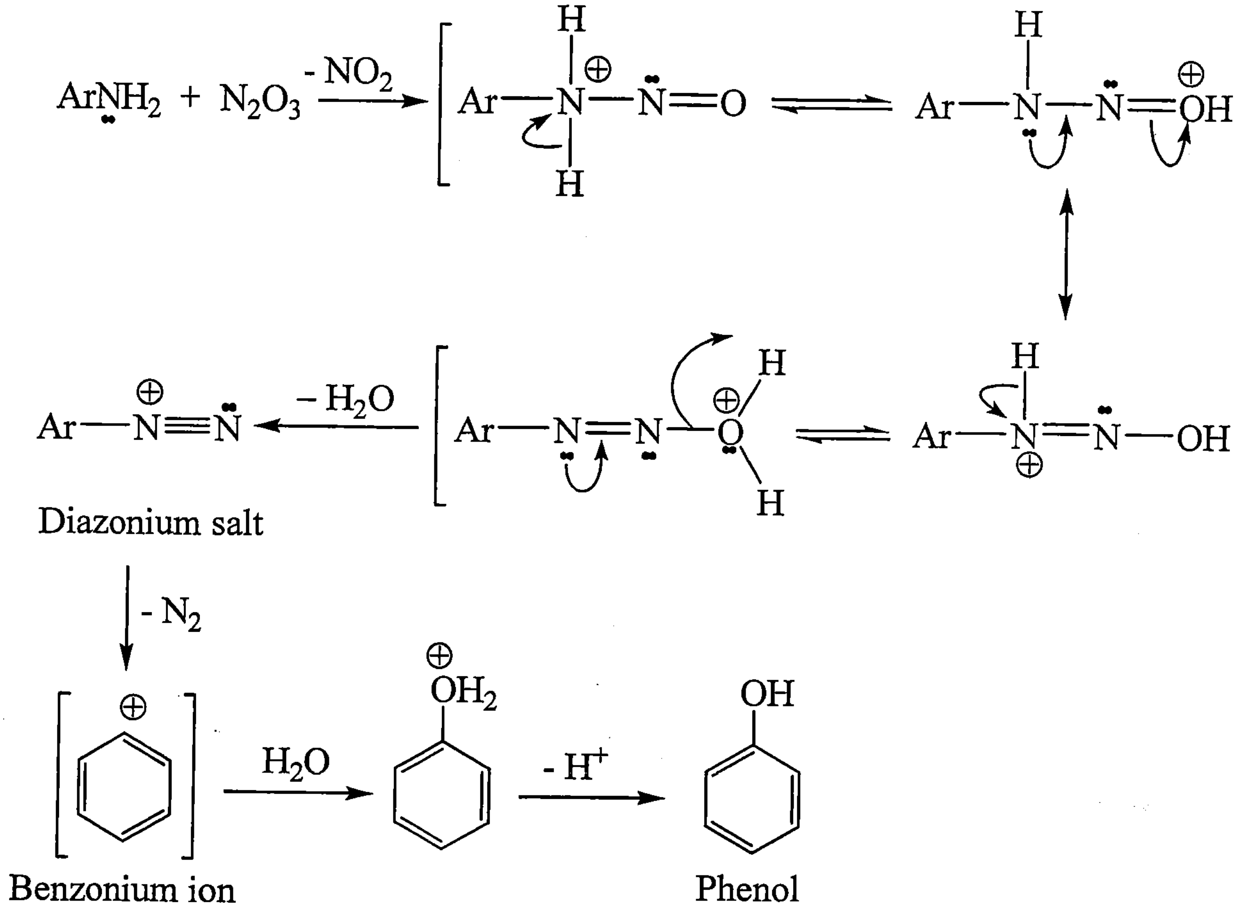


Reactions of Diazonium salts :



Mechanism :

$$2\,HONO \longrightarrow N_2O_3 + H_2O$$



Diazonium salt

Benzonium ion

Phenol

Theoretical calculations table :

Reactants	Products	Vol.	Density	Wt.	M.wt.	n	m.p.	b.p.
Aniline	---	2 mL	1.02	2.04	93	0.021	- 6	184
β - Naphthol	---	---	---	0.1	144	0.00069	123	286
---	Azo dye							
---	Phenol							

Calculation of percentage yield of the product :

$$\% = \frac{\text{no. of moles of the product}}{\text{no. of moles of the reactant}} \text{ X } 100$$

Procedure :

1st. week

1) To (2 mL) of aniline and (10 mL) of water in a (100 mL) conical flask , add with cooling (6 mL) of concentrated hydrochloric acid and cool the resulting solution to (0°C) in an ice bath (Fig. 5) .

2) Stir the solution continuously and slowly add an ice cold solution of (1 g.) of sodium nitrite in (10 mL) of water (Fig. 6) , making sure that the temperature of the reaction mixture does not rise above (5°C) during the addition . The resulting solution will be used for the next two parts of this experiment .

3) To (0.1 g.) of β – naphthol dissolved in (10 mL) of 10% sodium hydroxide solution , add with cooling and stirring (2 mL) of the diazomium solution prepared above .

4) Collect the red dye by Buchner filtration .

5) Determination of melting point will be made after drying .

6) Weigh the product and calculate the percentage yield .

7) The residual solution of diazonium salt will be left to the next week .

2$^{nd.}$ week

In order to get phenol

8) Steam distill the residual solution of the diazonium salt until we get a clear distillate (as shown in Fig. 2) .

9) Transfer the distillate to a separatory funnel and extract phenol with (15 mL) of ether .

10) Remove the aqueous layer and place the ether layer in (25 mL) conical flask and dry with anhydrous magnesium sulphate .

11) Filter the ether in previously weighed dry (25 mL) conical flask and remove the ether by evaporation on a water bath and weigh the residual liquid (phenol) then calculate the percentage yield .

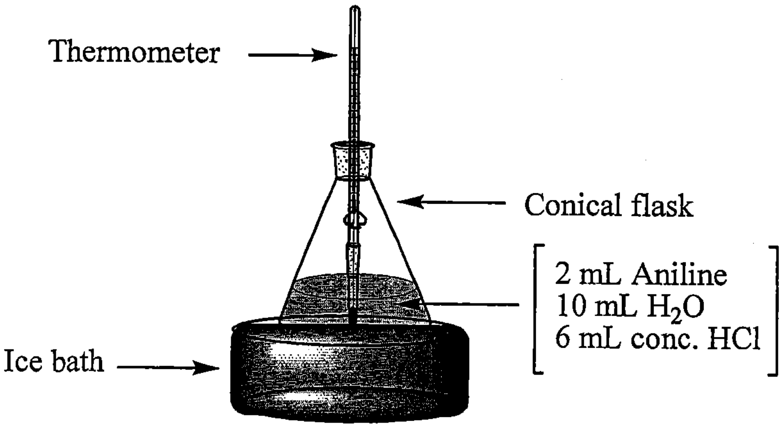


Fig. (5)

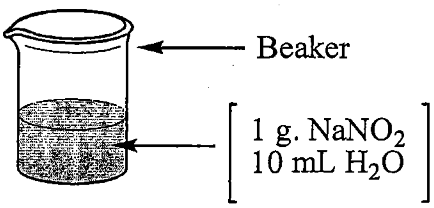
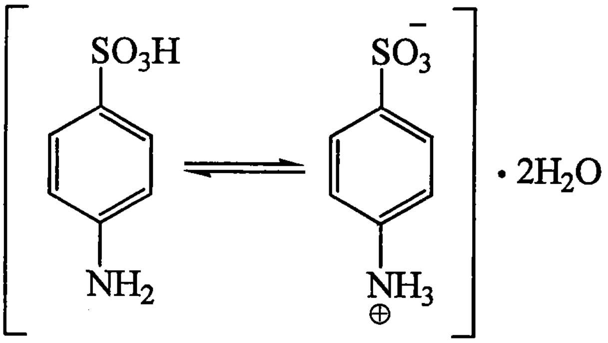


Fig. (6)

Sulphonation of Aniline

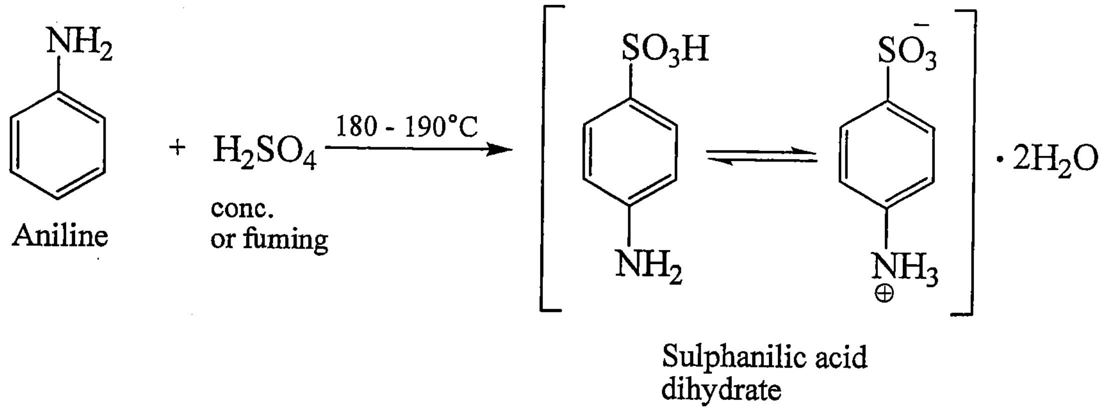
(Sulphanilic acid)

Theory : Sulphonation of aromatic compounds can be done by the use concentrated or fuming sulphuric acid . The sulphonatig agent is the sulpher trioxide (SO_3) the strong electrophilic agent . In this experiment (Sulphonation of aniline) , when aniline treated with an excess of concentrated sulphuric acid , it will afford a mixture that contain aniline sulphate . Heating of the latter up to 180°C will give *p*–aminobenzenesulphonic acid or (sulphanilic acid) and this separates as the zwitterions upon pouring the cooled mixture into a small amount of ice . The free acid will be in an equilibrium with the zwitterions (dipolar ion) form as shown bellow :

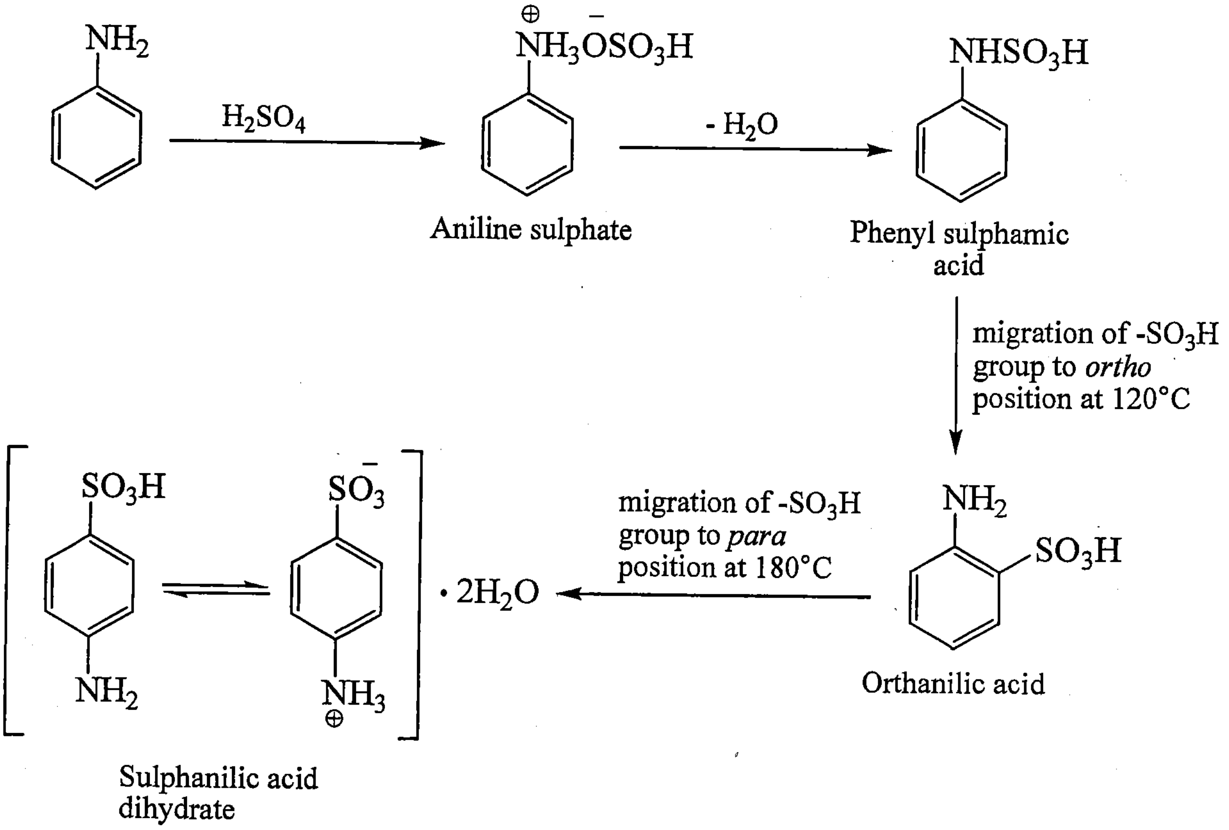


The reaction mechanism involve the loss of water molecule from aniline sulphate resulting in the formation of phenyl sulphamic acid . Rising the temperature will cause the migration of the ($-SO_3H$) group to the *ortho* position to give the orthanilic acid . At a higher temperature (180°C) , orthanilic acid convert to sulphanilic acid through the migration of ($-SO_3H$) group to the *para* position . The latter compound present in an equilibrium with the zwitterions .

General equation :



Mechanism :



Theoretical calculations table :

Reactants	Products	Vol.	Density	Wt.	M.wt.	n	m.p.	b.p.
Aniline	---	2 mL	1.02	2.04	93	0.021	- 6	184
---	Sulphanilic acid							

Calculation of percentage yield of the product :

$$\% = \frac{\text{no. of moles of the product}}{\text{no. of moles of the reactant}} \text{ X } 100$$

Procedure :

Note : All equipments must be clean and dry .

1$^{st.}$ week

1) In a (100 mL) round bottomed flask fitted with an air condenser , place (2 mL) of aniline and (8 mL) of concentrated sulphuric acid portion wise .

2) Heat the reaction mixture in a sand bath (Fig. 7) at (180 - 190°C) for at least (2.5 hours) then cool and leave it to the next week .

2$^{nd.}$ week

3) Pour the solution carefully with stirring into (50 g.) of crushed ice contained in a (400 mL) beaker .

4) Allow to stand for (10 minutes) , and collect the precipitated sulphanilic acid on a Buchner funnel , wash it well with water and drain .

5) Dissolve the crude product in a minimum volume of boiling water ; if the resulting solution is coloured , add decolourising carbon and boil the solution . Filter through a hot funnel and flask which have been preheated by the filtration of boiling distilled water . Upon cooling the dihydrate product

separates in colourless crystals . Filter and dry the crystals then determine the melting point (decomposition) .

6) Weigh the product and calculate the percentage yield .

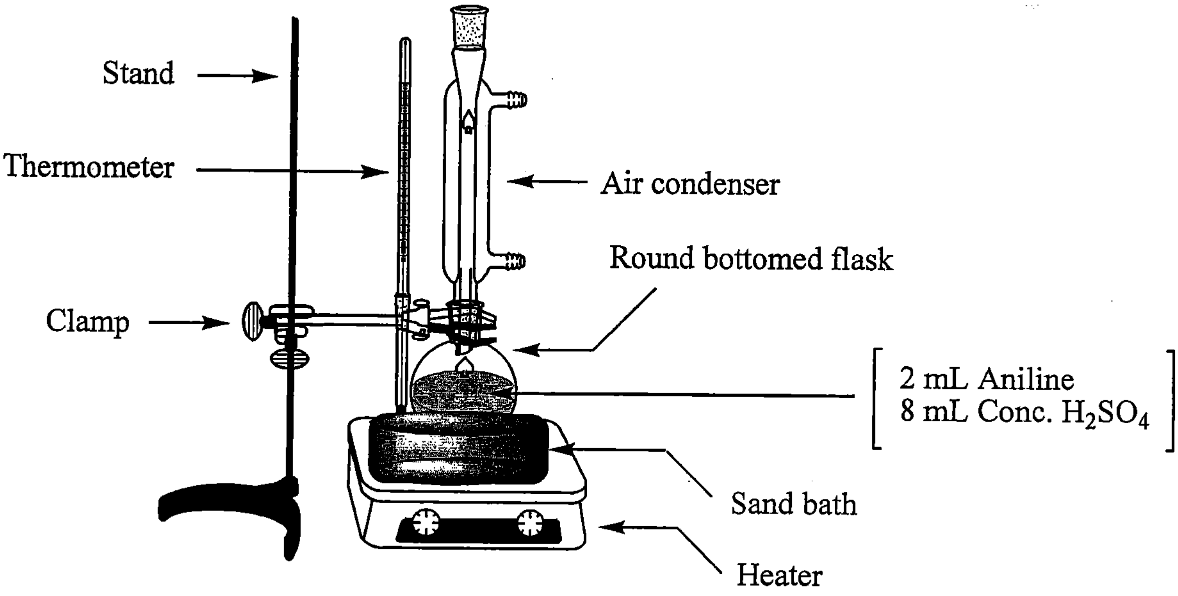


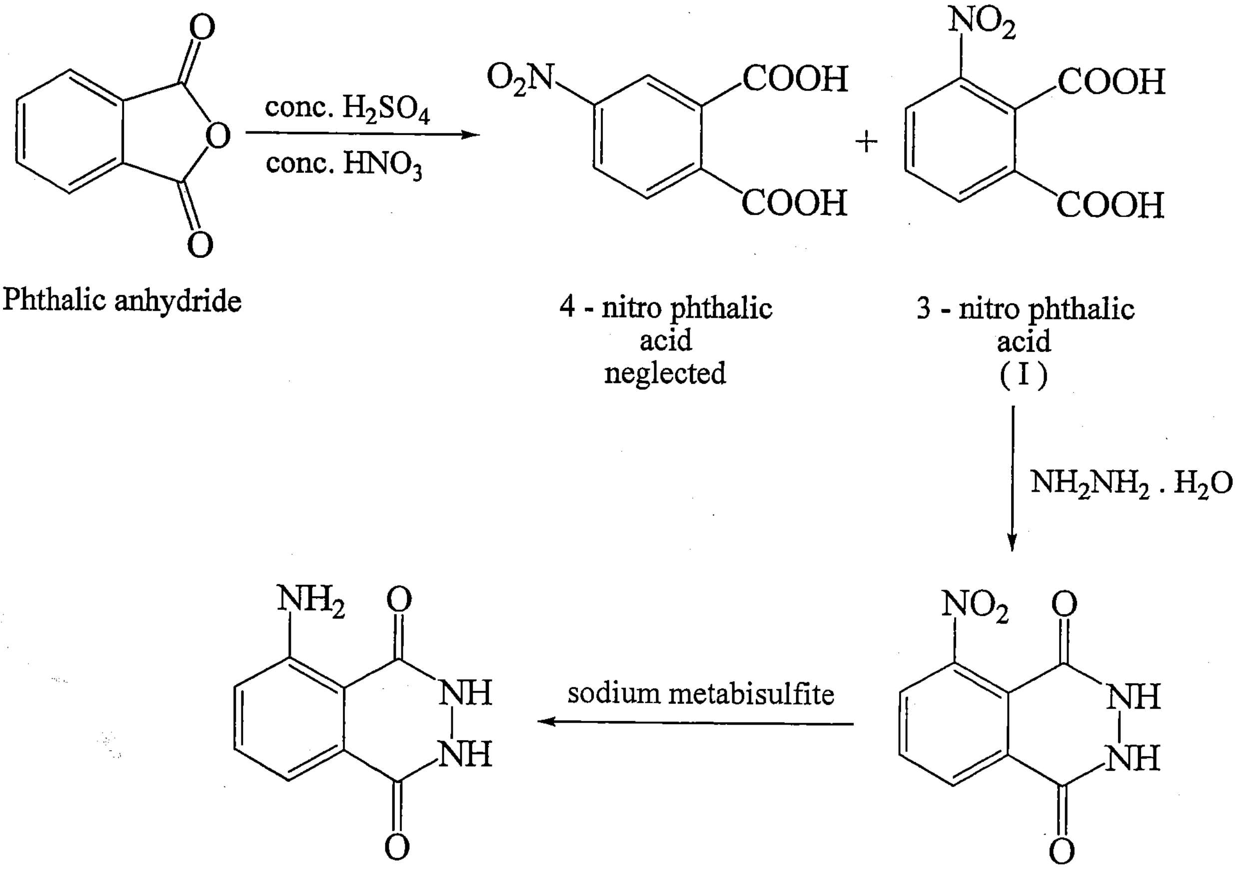
Fig. (7)

Synthesis of Luminol

Theory : Cyclic compounds that contain hetero atoms like (sulfur , nitrogen and / or oxygen) beside carbon atoms are known as heterocyclic compounds which were widely spread in nature .

In this experiment , the chemiluminscent compound (5 – amino - 2,3 - dihydro - 1,4 - phthalazine dione) which is known as luminol , will be synthesized by the reduction of the nitro derivative (II) that formed on thermal dehydration (loss of two water molecules) of a mixture of 3 – nitrophthalic acid (I) and hydrazine . Nitrophthalazine dione (II) , is insoluble in dilute acid but soluble in alkali , since it convert to the ionic form which is conveniently reduced to luminol (III) by sodium metabisulfite in alkaline solution .

General equation :



Phthalic anhydride

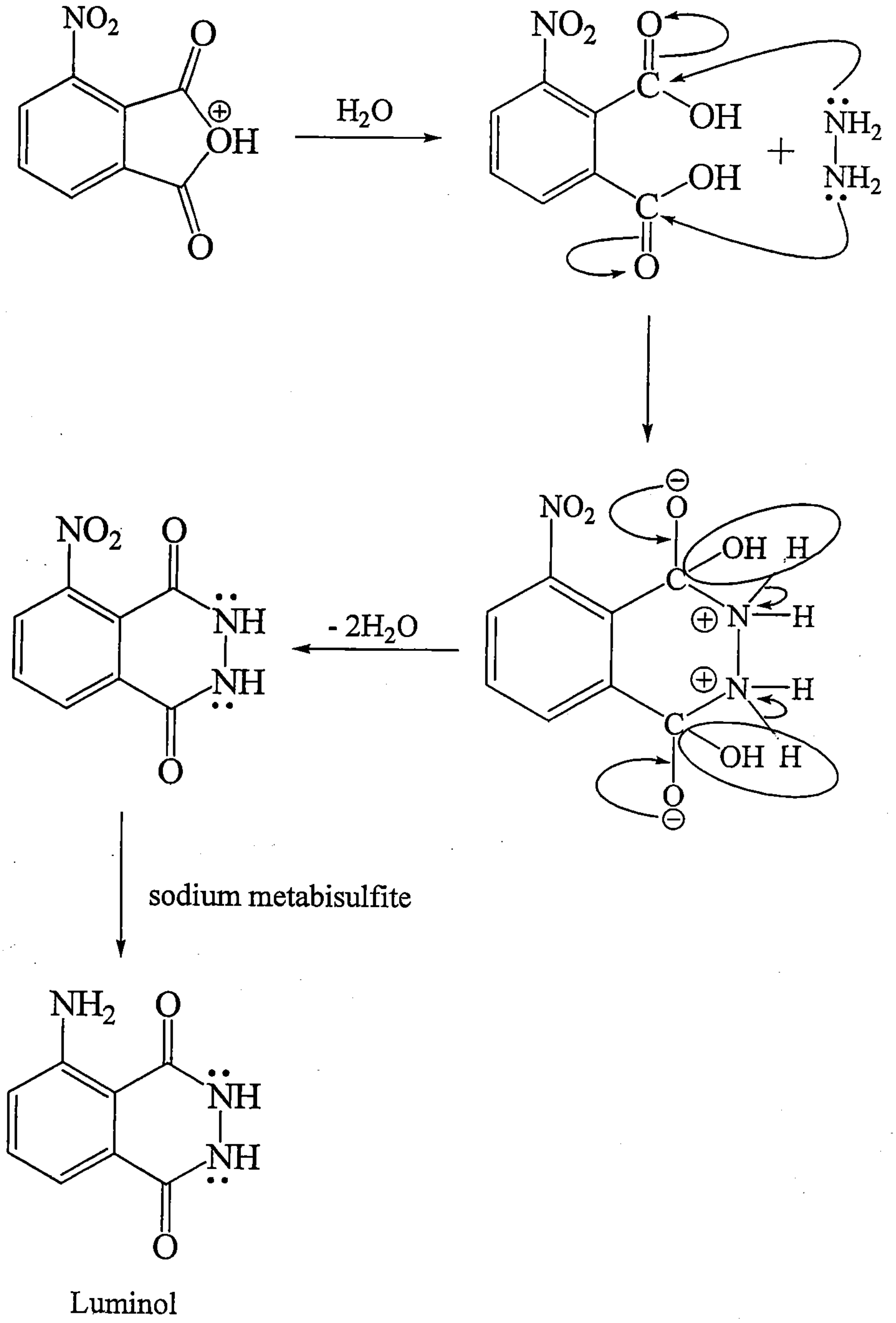
4 - nitro phthalic acid neglected

3 - nitro phthalic acid (I)

Luminol (III)

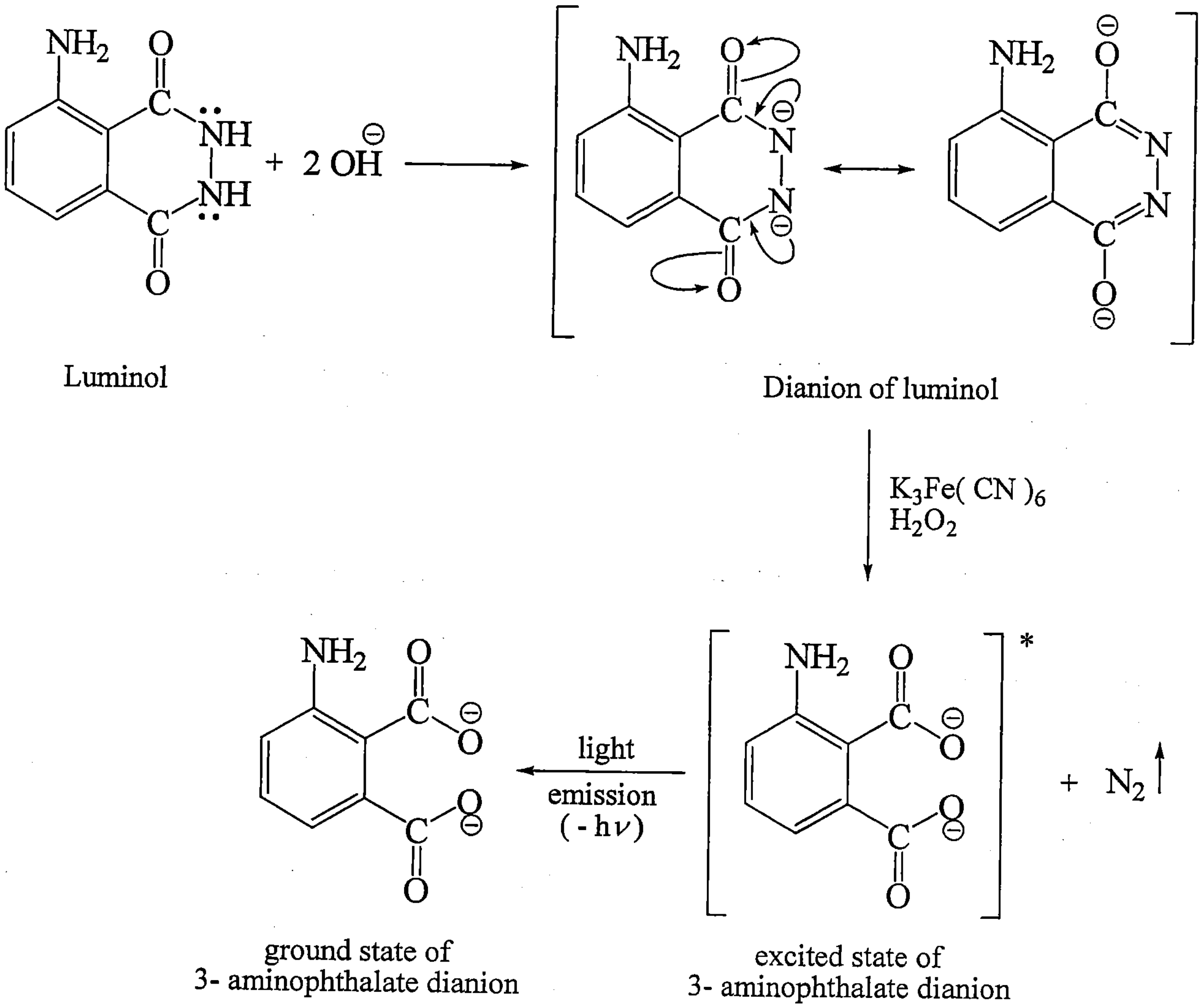
(II)

Mechanism :



Detection of luminol :

Treatment of the alkaline solution of luminol with a mixture of potassium ferricyanide and hydrogen peroxide (as oxidizing agent) will produce 3- amino phthalate dianion in an electronically excited state . The excited dianion emits a photon that is visible as a light (blue – green light) . This phenomenon is called chemilumenscence (Fluorescence) .



Theoretical calculations table :

Reactants	Products	Vol.	Density	Wt.	M.wt.	n	m.p.	b.p.
Phthalic anhydride	---	---	---	6.25	148	0.042	131 - 134	284
---	3 – nitro phthalic acid							
Nitro der.	---	---	---	0.7	207	0.0033	> 300	---
---	luminol							

Calculation of percentage yield of the product :

$$\% = \frac{\text{no. of moles of the product}}{\text{no. of moles of the reactant}} \text{ X } 100$$

Procedure :

Note : All equipments must be clean and dry .

1st. week

1) Place (0.25 g.) of phthalic anhydride in a (250 mL) three – necked flask fitted with a dropping funnel and reflux condenser (Fig. 8) .

2) Place (8 mL) of concentrated sulphuric acid in the dropping funnel .

3) Run in the sulphuric acid in one portion to the phthalic anhydride with stirring and heat the mixture on a water bath until all the solid dissolved .

4) Place (15 mL) of concentrated nitric acid in the dropping funnel .

5) Run in the nitric acid drop wise in such a rate that the temperature doesn't rise above (100 – 110°C) .

6) Heating and stirring must be continued for (2 hrs.) with continuous stirring .

7) Cool the reaction mixture and transfer it into flat bottomed flask and stopper it securely .

2nd. week

8) Pour the content of the flask (3 – nitrophthalic acid and 4 – nitrophthalic acid) into (75 mL) of cold water in a beaker with stirring in order to get rid of 4 – nitrophthalic acid (soluble in cold water).

9) Filter the solid (3 – nitrophthalic acid) at Buchner and wash it with cold water .

10) Recrystallize the product from boiling water .

11) Determination of melting point will be made after drying .

12) Weigh the product and calculate the percentage yield .

3rd. week

13) Place (1 g.) of 3 – nitrophthalic acid and (2 mL) of hydrazine hydrate in a (20 * 150 mm) test tube (Fig. 9) , and heat the mixture until the solid dissolve .

14) Add (3mL) of triethylene glycol , and clamp the tube in a vertical position in a hot sand bath or heating mantle .

15) Insert a thermometer and two boiling chips and heat the solution to (100 - 130°C) .

16) Let the temperature rise rapidly until reaches (215°C) during (3 – 4 min.) .

17) With gentle heating , maintain the temperature at (220°C) for (2 min.) then remove the tube and let it to cool to about (100°C) .

18) Add (15 mL) of hot water , cool under the tap and collect the light yellow granular nitro compound by Buchner filtration .

19) In order to reduce the nitro compound , transfer (0.7 g.) of the nitro compound (which need not be dried) to the uncleaned test tube in which it was prepared .

20) Add (5 mL) of 10% of sodium hydroxide solution , stir with a road , and to the resulting deep brown – red solution add (3 g.) of sodium metabisulfite ($NaHSO_3$) .

21) Wash the solid down the walls of the tube with a little amount of water , then heat on a heater to the boiling point with stirring and keep the mixture hot for (5 min.) .

22) Add (2 mL) of acetic acid and cool the test tube under the tap then stopper it securely to the next week .

4th. Week

23) Leaving the reaction mixture to stand overnight deposits a further crop of luminol .

24) Collect the resulting precipitate by Buchner filtration .

25) Determination of melting point will be made after drying .

26) Weigh the product and calculate the percentage yield .

Test for Luminol :

1) Dissolve the first crop of moist luminol (dry weight 0.2 – 0.3 g.) in (10 mL) of 10% sodium hydroxide solution and (20 mL) of water (stock solution A) .

2) Prepare a second stock solution (B) , by mixing (20 mL) of 3% potassium ferricyanide , (20 mL) of 3% hydrogen peroxide and (60 mL) of water in a (250 mL) conical flask .

3) Pour solution A onto solution B (in a dark place) in the conical flask and swirl the flask and watch the blue – green fluorescence of luminol .

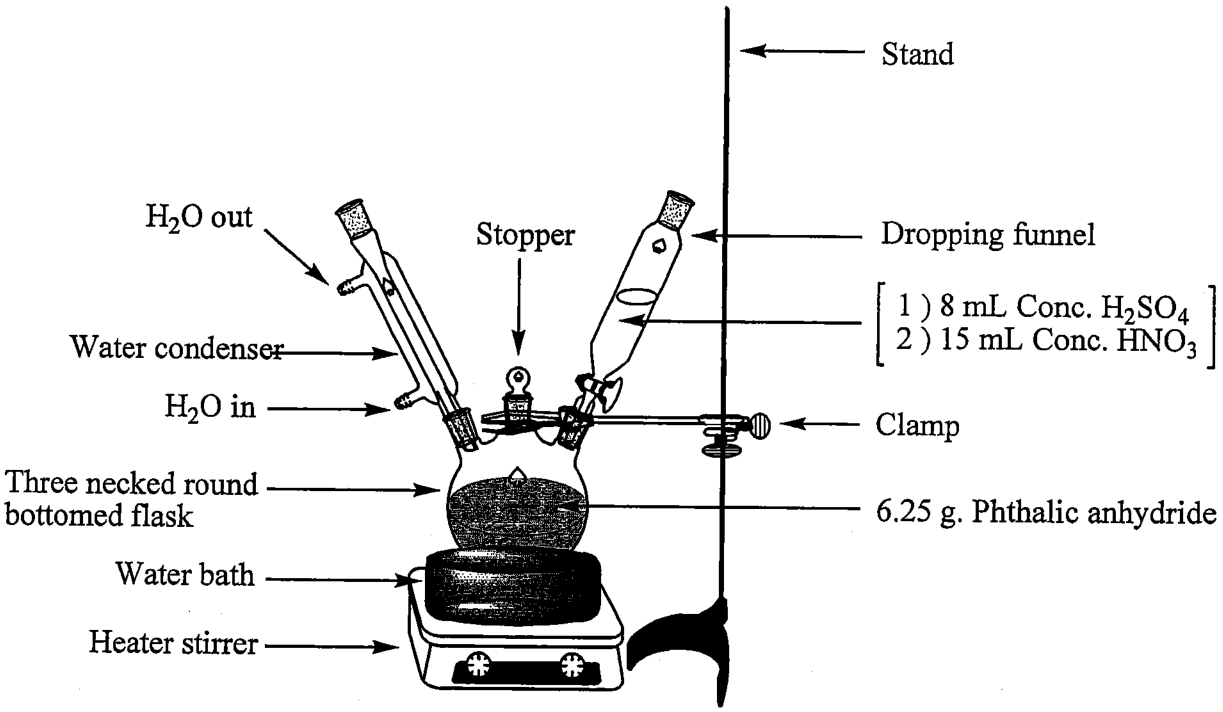


Fig. (8)

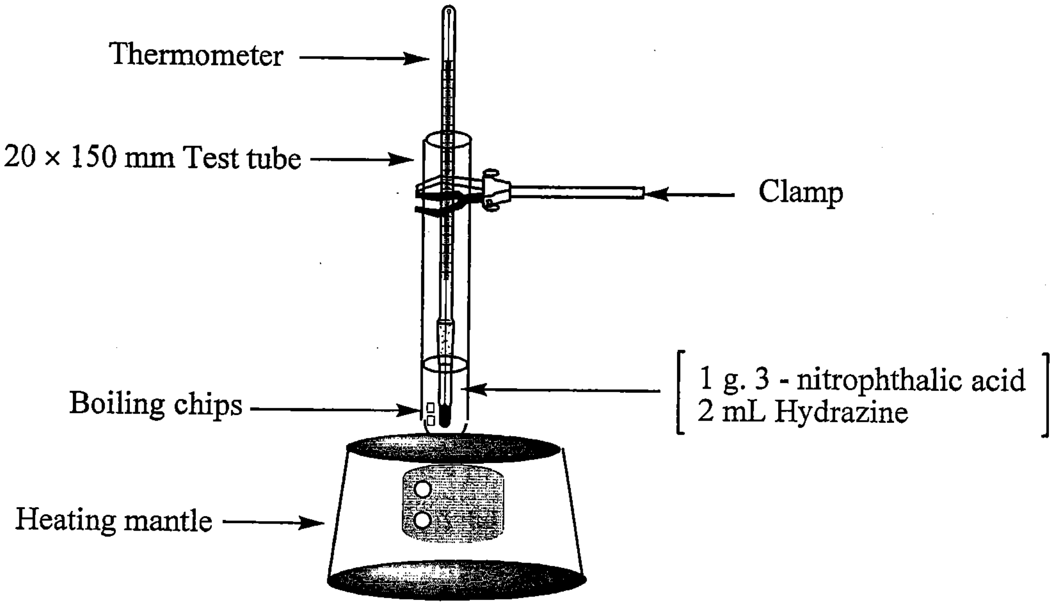


Fig. (9)

Pinacol - Pinacolone rearrangement

Theory : Acetone is reduced by amalgamated magnesium largely to bimolecular reduction product , tetramethylethylene glycol or **pinacol** ; some isopropyl alcohol is also formed .

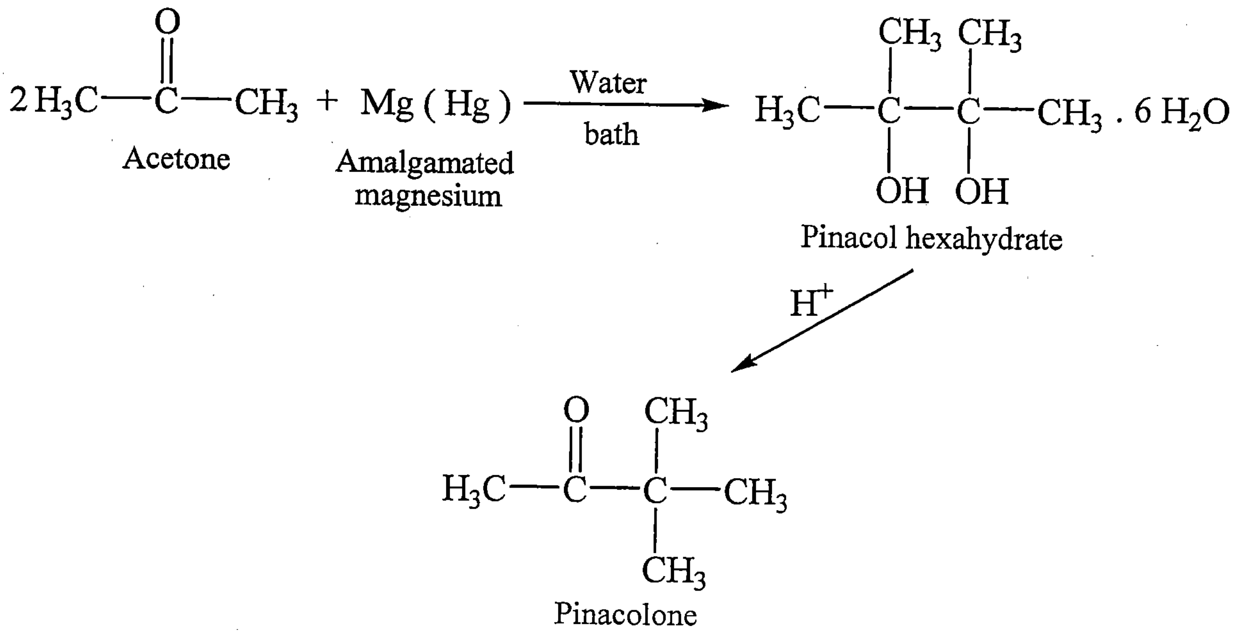
The magnesium is conveniently amalgamated by dissolving mercuric chloride in a portion of the acetone ; mercury is then liberated by the reaction :

$$HgCl_2 + Mg \longrightarrow Hg + MgCl_2$$

Pinacol upon dehydration with acid catalysts (*e.g.* sulphuric acid) is transformed into methyl *tert.* – butyl ketone or pinacolone . This arrangement , known as the **pinacol – pinacolone rearrangement** , which involve shifting of methyl group from one of the glycol carbon atoms to the other (1,2 methyl group shift) .

General equation :

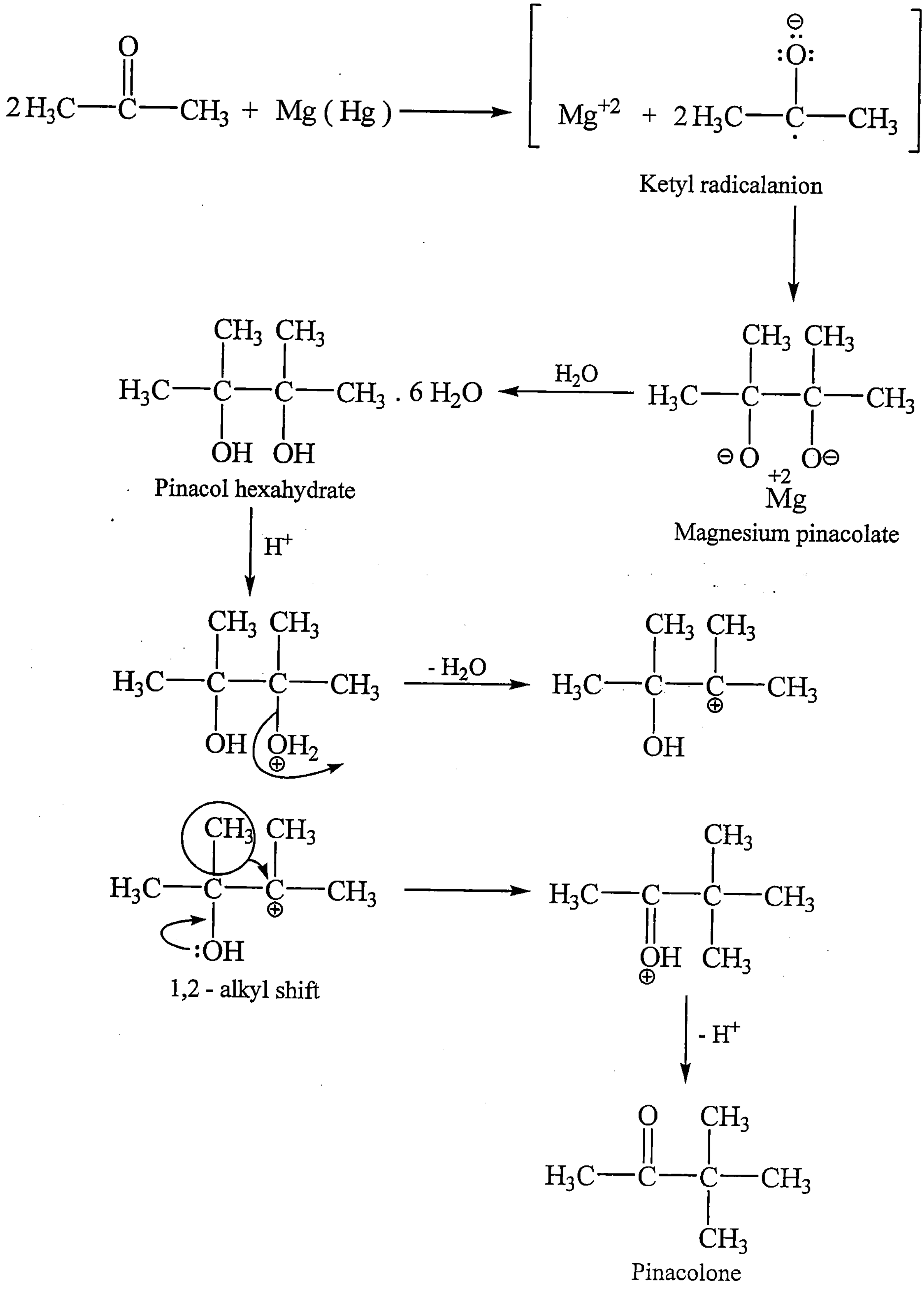
$$\underset{\text{Mercuric chloride}}{HgCl_2} + \underset{\text{Magnesium}}{Mg} \longrightarrow \underset{\text{Amalgamated magnesium}}{Mg(Hg)} + MgCl_2$$



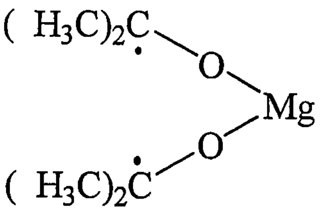
$$2\,H_3C-\overset{\overset{O}{\|}}{C}-CH_3 + Mg(Hg) \xrightarrow[\text{bath}]{\text{Water}} H_3C-\underset{\underset{OH}{|}}{\overset{\overset{CH_3}{|}}{C}}-\underset{\underset{OH}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_3 \cdot 6\,H_2O \xrightarrow{H^+} H_3C-\overset{\overset{O}{\|}}{C}-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_3$$

Mechanism :

A) By the formation of ketyl radical anion :



B) By the formation of free radical only :



Note that both routs (A & B) resulting in the formation of magnesium pinacolate .

Theoretical calculations table :

Reactants	Products	Vol.	Density	Wt.	M.wt.	n	m.p.	b.p.
Acetone	---	15 mL	0.791	11.8	58	0.203	- 94	56
---	Pinacol hexahydrate							
---	Pinacolone							

Calculation of percentage yield of the product :

$$\% = \frac{\text{no. of moles of the product}}{\text{no. of moles of the reactant}} \quad X\ 100$$

Procedure :

Note : All equipments must be dry and clean .

1) In a (100 mL) round bottomed flask , fitted with a reflux condenser and a dropping funnel (Fig. 10) . Place (0.5 g.) of dry magnesium metal and (15 mL) of dry benzene .

2) Place a solution of (0.5 g.) of mercuric chloride in a (15 mL) of dry acetone in the dropping funnel and run about one quarter of this solution .

3) If the reaction does not commence in a few minutes , as indicated by vigorous ebullition , warm the flask on a water bath .

4) Once the reaction has started , no further heating is required .

5) Add the remainder of the solution dropwise at such a rate that the reaction is as vigorous as possible and yet under control .

6) When the reaction slow down , warm the flask on a water bath for (45 min.) .

7) Magnesium pinacolate will be formed after the completion of the reaction .

8) Add (10 mL) of water through the condenser and heat again on a water bath for (15 min.) . This will convert the magnesium pinacolate into pinacol hydrate .

9) Filter the solution at the pump to remove insoluble magnesium hydroxide and keep the filtrate in a (50 mL) flat bottomed flask to the next week .

2^{nd.} week

10) Concentrate the solution to one third the original volume in water bath .

11) Place the residual solution in (100 mL) round bottomed flask fitted with a condenser (Fig. 11) and add about (15 mL) of water , (4 mL) of concentrated sulphuric acid and tow pieces of boiling chips .

12) reflux the mixture for (15 min.) .

13) Distil the mixture and neglect the first (100 – 120) drops then collect about (2 mL) of the distillate (pinacolone) in a test tube and make sure that distillation should not be achieved to dryness .

Chemical test for pinacolone :

1) Add about (3 – 4) drops of 2,4 – dinitrophenyl hydrazine solution to the collected pinacolone .

2) Shake the test tube well .

3) The appearance of yellow precipitate indicate the presence of carbonyl group (2,4 – dinitrophenyl hydrazone derivative of pinacolone) .

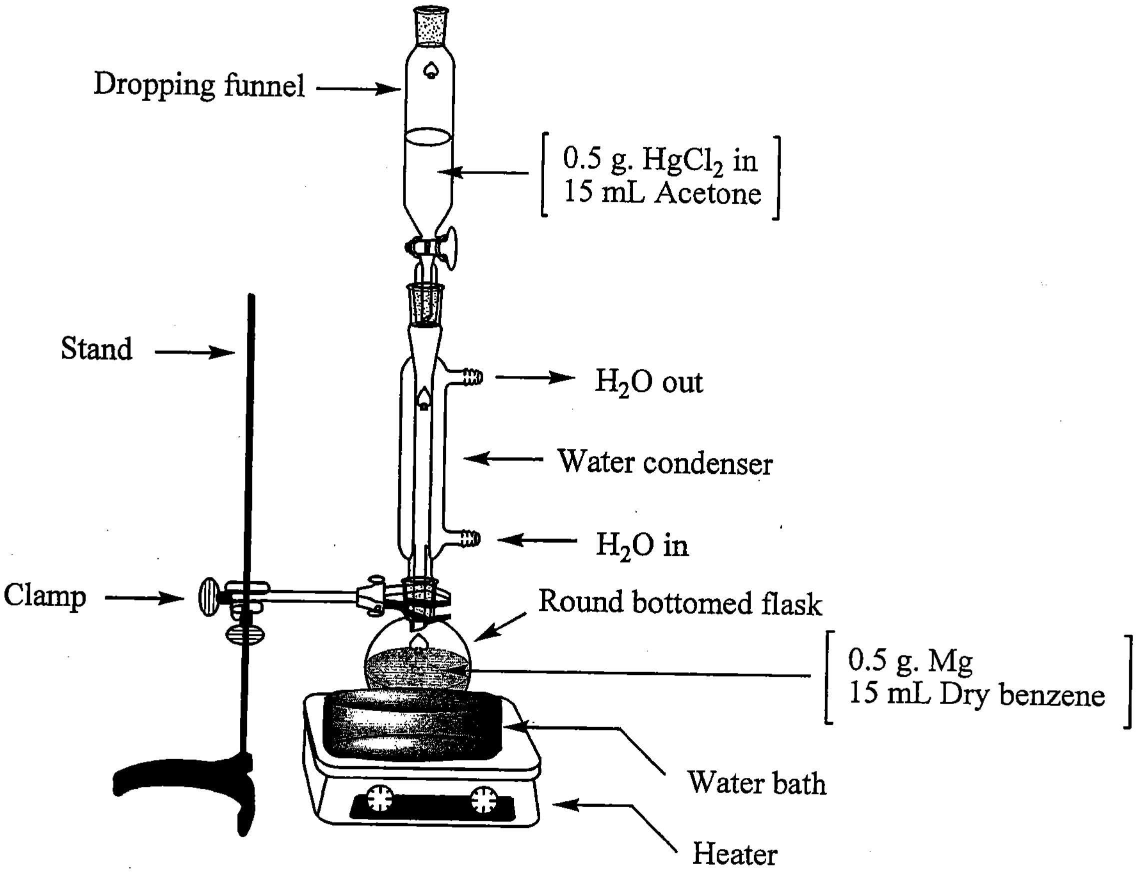

Dropping funnel
0.5 g. $HgCl_2$ in
15 mL Acetone
Stand
H_2O out
Water condenser
H_2O in
Clamp
Round bottomed flask
0.5 g. Mg
15 mL Dry benzene
Water bath
Heater

Fig. (10)

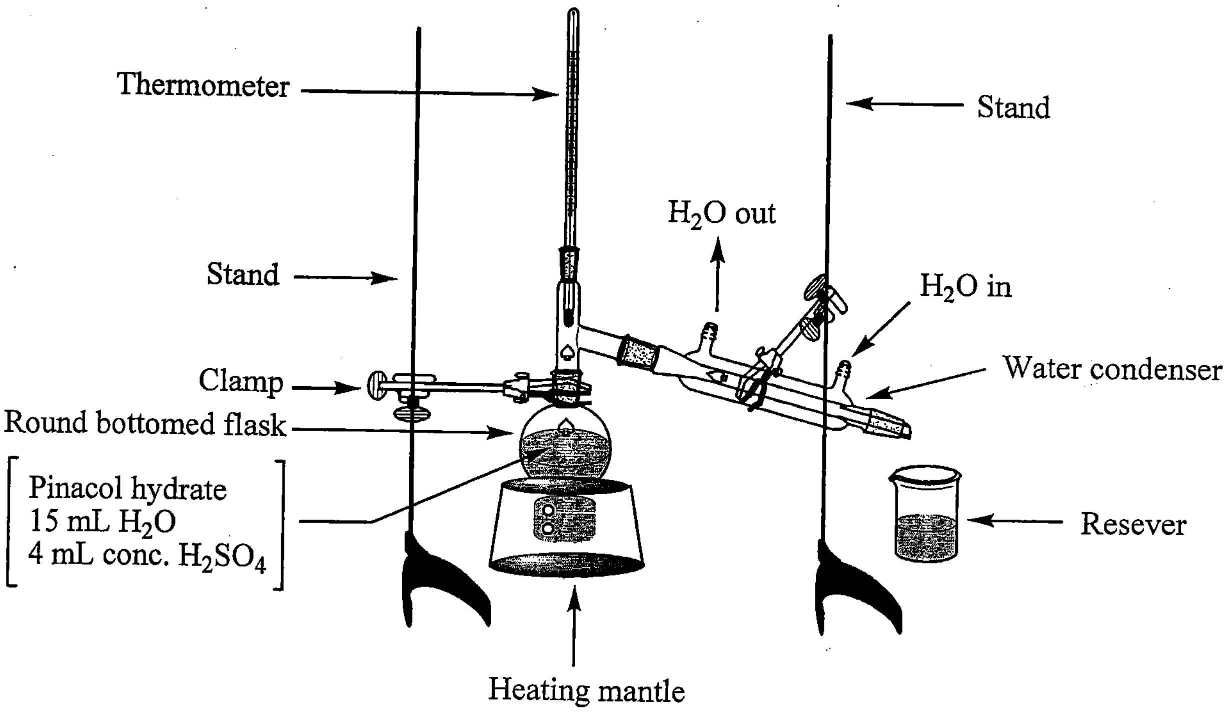
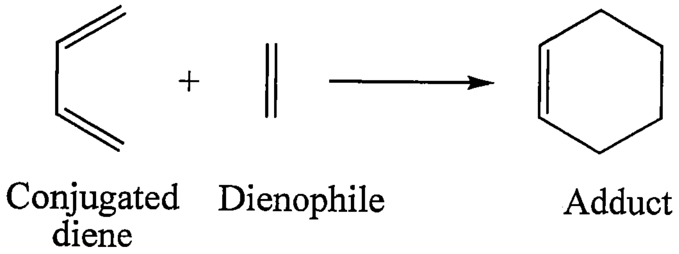

Thermometer
Stand
H_2O out
Stand
H_2O in
Clamp
Water condenser
Round bottomed flask
Pinacol hydrate
15 mL H_2O
4 mL conc. H_2SO_4
Resever
Heating mantle

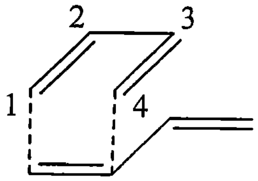
Fig. (11)

Diels – Alder reaction

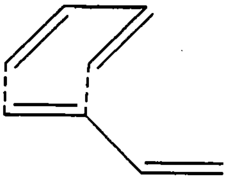
Theory : α , β – unsaturated carbonyl compounds undergoes one of the most important reaction with conjugated dienes which must adopt the (cis) form resulting in the formation of six membered cyclic system . This reaction is known as Diels – Alder reaction in which the double bound of the dienophile will be add to the ends of the conjugated diene which known as 1,4 – cycloaddition (or 4 + 2 cycloaddition) .



The endo addition is preferred on the exo , since most of the addition products in Diels – Alder reaction adopt the endo stereochemistry due to the overlap between π orbitals of the carbon carbon bond that form in the product with those of the dienophile , thus the energy that required to reach to the transition state will be decreased .

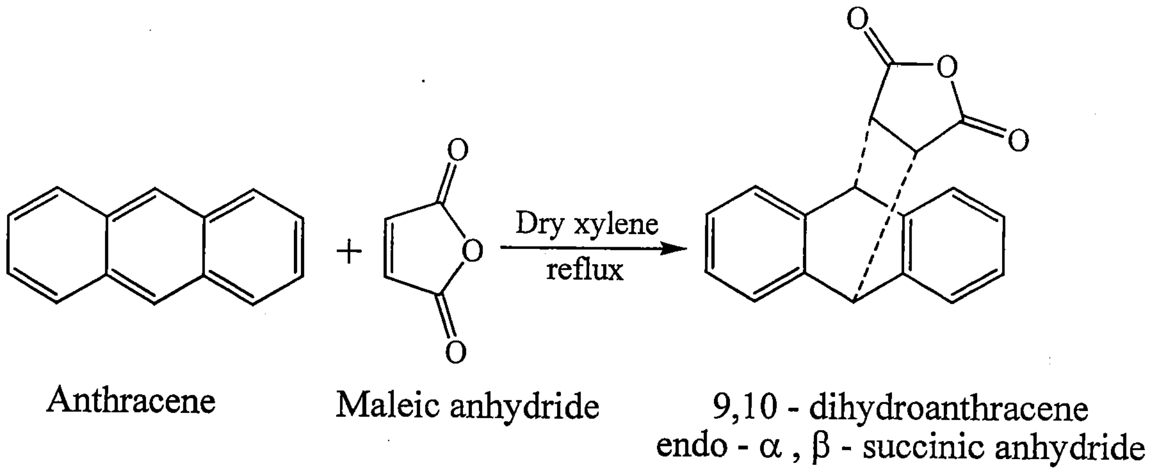


endo - adduct
Sin



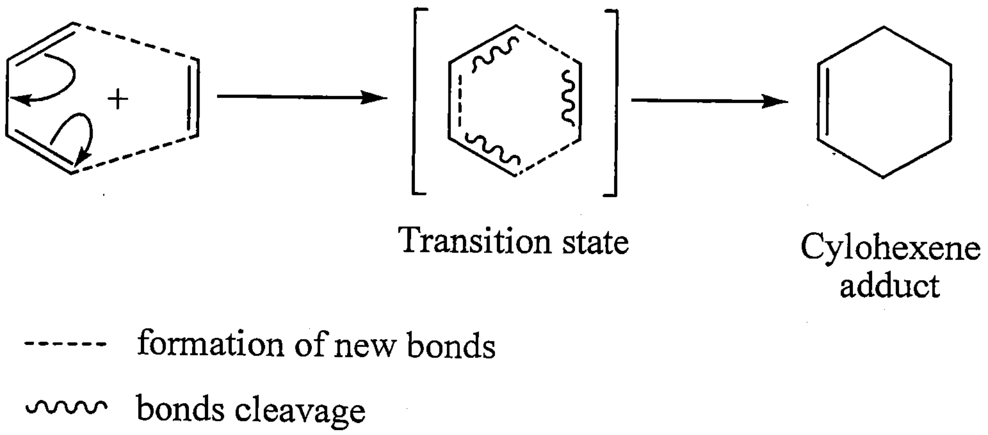
exo -adduct

General equation :



Mechanism :

A) Single step (simultaneous) addition :



B) Two steps ionic or free radical reaction .

Theoretical calculation table :

Reactants	Products	Vol .	Density	Wt .	M.wt.	n.	m.p.	b.p.
Anthracene	---	---	---	0.5	178	0.0028	216	340
Maleic anhydride	---	---	---	0.3	98	0.003	54	200
---	Adduct							

Calculation of percentage yield of the product :

$$\% = \frac{\text{no. of moles of the product}}{\text{no. of moles of the reactant}} \text{ X } 100$$

Procedure :

Note : All equipments must be dry and clean .

1) In a (100 mL) round bottomed flask fitted with reflux condenser , place (0.5 g.) of anthracene , (0.3 g.) of maleic anhydride , (20 mL) of dry xylene and two pieces of boiling chips (Fig. 12) .

2) Boil the mixture under reflux for (20 min.) .

3) Allow the mixture to cool .

4) Collect the solid that separate on cooling and scratching by filtration .

5) Determination of melting point will be made after dryness .

6) Weigh the product and calculate the percentage yield .

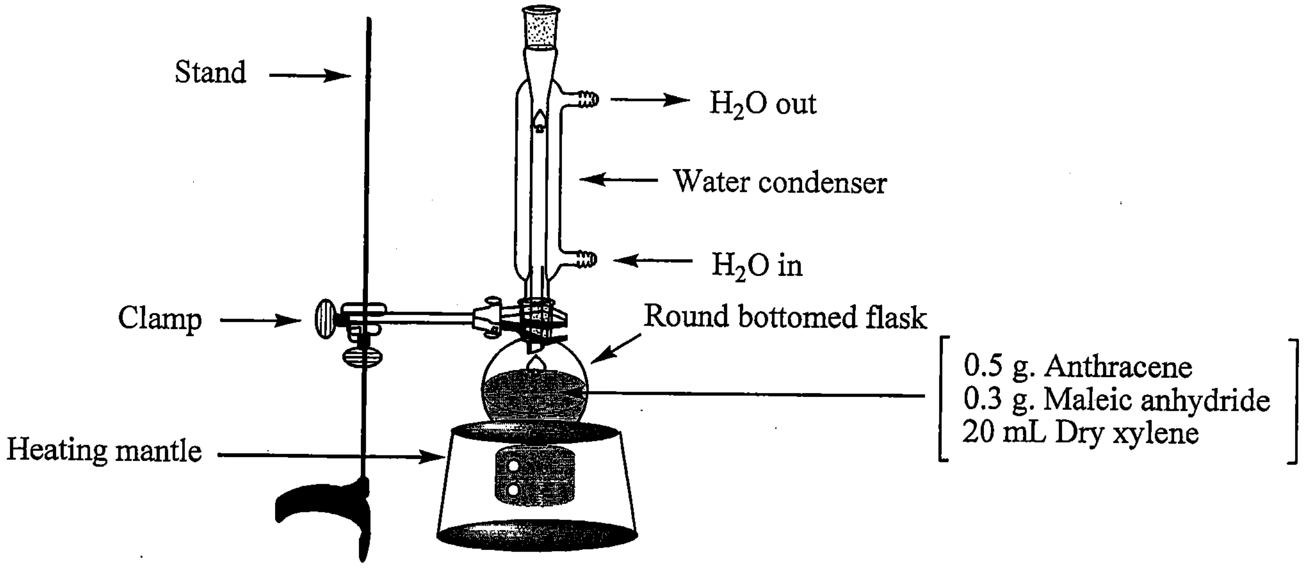

Stand
H_2O out
Water condenser
H_2O in
Clamp
Round bottomed flask
0.5 g. Anthracene
0.3 g. Maleic anhydride
20 mL Dry xylene
Heating mantle

Fig. (12)

Grignard Reagent

Theory : Organometalic compounds represent an important methods in organic synthesis . Magnesium metal can react with most of alkyl or aryl halides (except fluorides) in the presence of weak basic solvent like dry ether or tetrahydrofurane (THF) to form Grignard reagent .

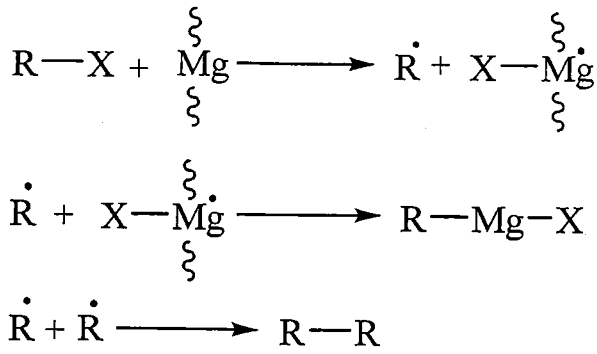
$$RX + Mg \xrightarrow{\text{dry ether}} RMgX$$

Synthesis of Grignard reagent must be done under anhydrous conditions , thus all equipments and reagents must dry since presence of water prevent the reaction from start , moreover it will decompose the reagent since it react easily with the reagent as the following :

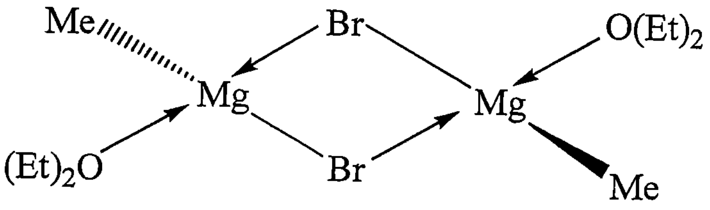
$$RMgX + H_2O \xrightarrow{\text{dry ether}} RH + Mg(OH)_2 + MgX_2$$

In addition to its reaction with water , Grignard reagent undergo a number of side reactions such as its reaction with oxygen or carbon dioxide and others.

This experiment involve the synthesis of phenyl magnesium bromide , reaction of the latter with ethyl benzoate will afford triphenyl methanol as a main product . In some cases , very little amounts of ketone (intermediate) can be separated even when we use an execs amount of ester and this can be attributed to the fact that ketone is more reactive than ester . Furthermore biphenyl will be produced as side product .

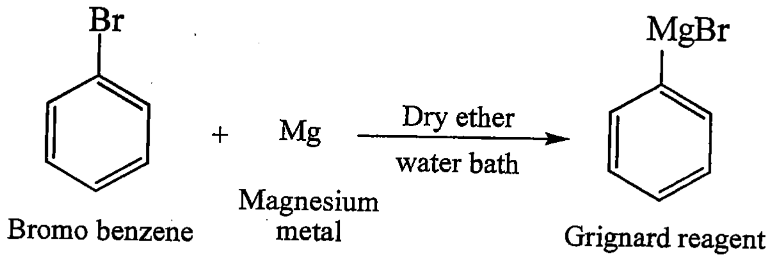


The structure of the reagent in ether :

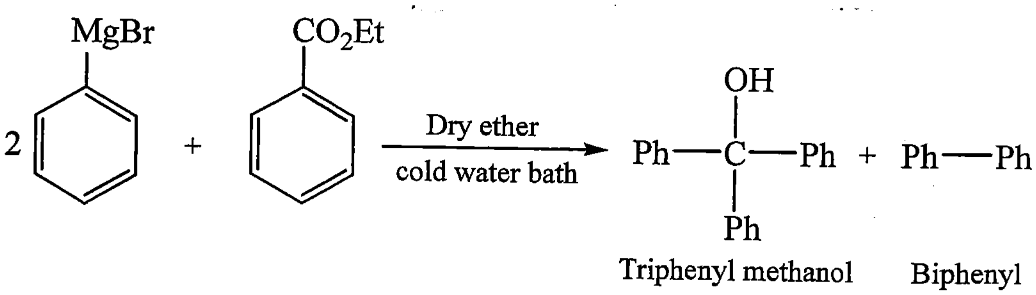


General equation :

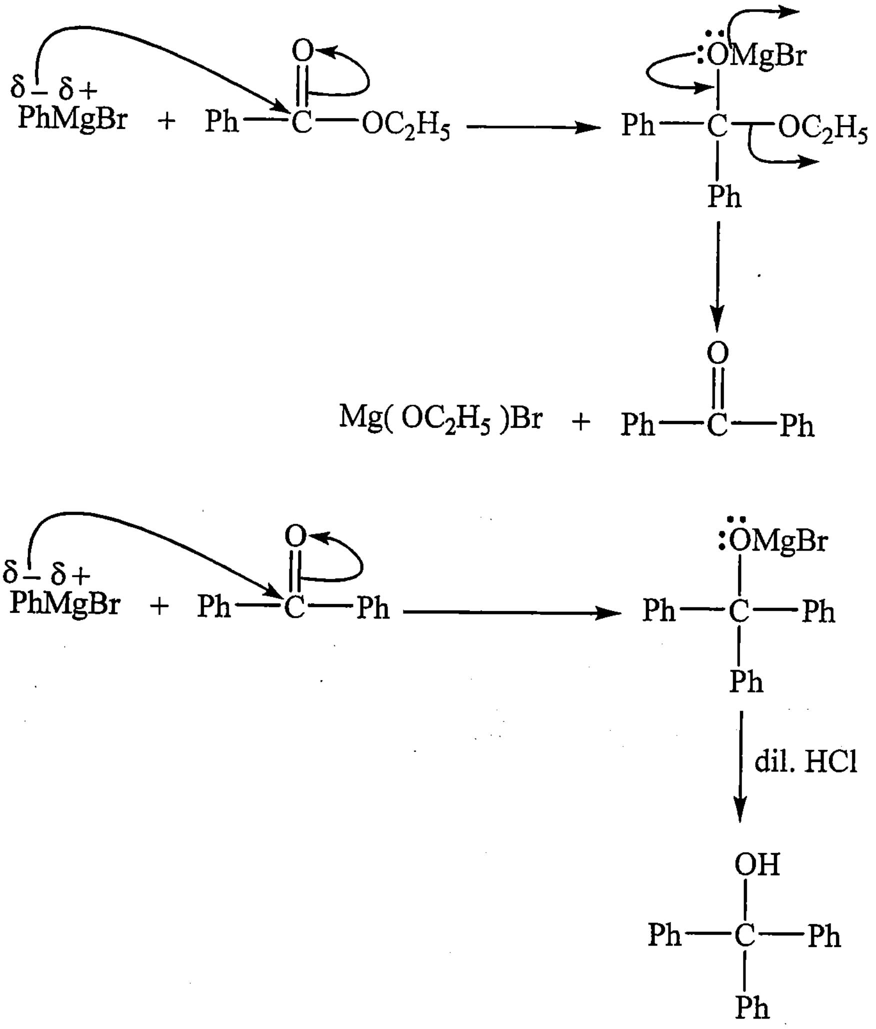
1)



2)



Mechanism :


δ– δ+
PhMgBr + Ph—C(=O)—OC$_2$H$_5$
Ph—C(Ph)(:Ö MgBr)—OC$_2$H$_5$
Mg(OC$_2$H$_5$)Br + Ph—C(=O)—Ph
δ– δ+
PhMgBr + Ph—C(=O)—Ph
Ph—C(Ph)(:Ö MgBr)—Ph
dil. HCl
Ph—C(Ph)(OH)—Ph

Theoretical calculations table :

Reactants	Products	Vol.	Density	Wt.	M.wt.	n	m.p.	b.p.
Ethyl or Methyl benzoate	---	3.6 mL	1.051	3.76	150	0.025	- 34	212
	Triphenyl methanol							

Calculation of percentage yield of the product :

$$\% = \frac{\text{no. of moles of the product}}{\text{no. of moles of the reactant}} \quad X\,100$$

Procedure :

Note : All equipments must be clean and dry .

1$^{st.}$ week

1) Place (0.5 g.) of dry magnesium metal and (20 mL) of sodium dried ether in a (250 mL) three necked flask fitted with a dropping funnel and a reflux condenser (Fig. 13) , then start to heat gently on a water bath with stirring .

2) Place a solution of (6 – 7 mL) of dry bromobenzene in (9 mL) of dry ether in the dropping funnel .

3) Run in the bromobenzene solution (about 3.75 mL) to the warm solution and wait for (15 min.) until the reaction becomes vigorous .

4) Run the residual solution in the dropping funnel dropwise to the cloudy solution .

5) Heating should be continued for further (15 min.) in order to ensure the completion of the reaction .

6) Cool the solution in an ice water bath and place a solution of (3.6 mL) of dry ethyl benzoate in (6.4 mL) of dry ether in the dropping funnel .

7) Add the ethyl benzoate solution dropwise to the resulting Grignard reagent (phenyl magnesium bromide) with cooling due to the exothermic reaction .

8) Heat the reaction mixture for (15 min.) .

9) In order to obtain the product , acidify with cooling the resulting solution (magnesium salt of triphenyl methanol) with diluted hydrochloric acid .

10) Transfer the resulting mixture to a separatory funnel and remove the water layer and place the ethereal layer in a (100 mL) flat bottomed flask , and stopper it securely with cork stopper .

2nd. week

11) Steam distil the solution (as shown in Fig. 2) in order to separate the biphenyl (bi product) .

12) Cool the residual solution and filter the solid (triphenyl methanol) at the pump .

13) Determination of melting point will be made after drying .

14) Weigh the product and calculate the percentage yield .

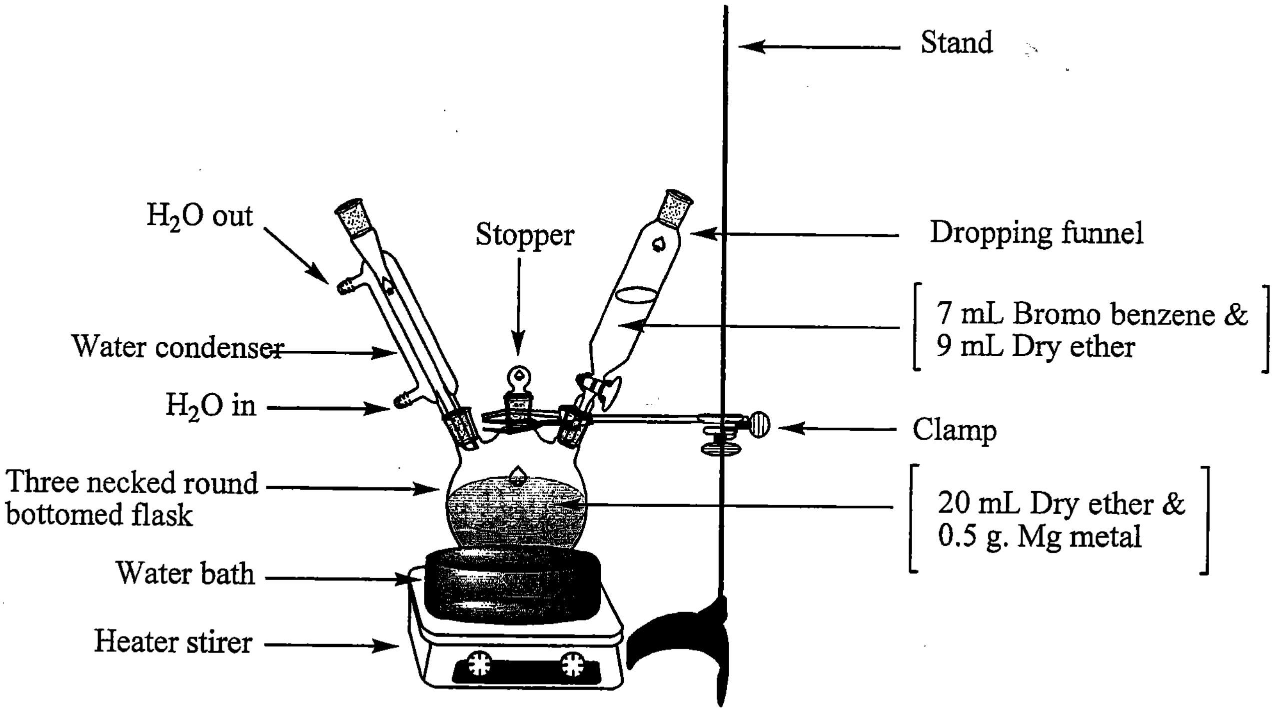

Stand
H$_2$O out
Stopper
Dropping funnel
7 mL Bromo benzene &
9 mL Dry ether
Water condenser
H$_2$O in
Clamp
Three necked round bottomed flask
20 mL Dry ether &
0.5 g. Mg metal
Water bath
Heater stirer

Fig. (13)

REFERENCES

1) A. I. Vogel , " A Text book of practical organic chemistry " , 5th. Edn. , Longman , London , 1987 .

2) H. Hart , " Laboratory Manual organic chemistry a short course " , 7th. Edn. , Houghton Mifflin company , U.S.A. , 1987 .

3) L. F. Fieser and K. L. Williamson , " Organic Experiments " , 7th. Edn. , D. C. Heath and company , U.S.A. , 1992 .

4) M. B. Smith and J. March , " March's advanced organic chemistry Reactions , Mechanisms and Structure " , 6th. Edn. , John Wiley & Sons , U.S.A. , 2007 .