



Organic Chemistry Laboratory

Part (II)



By:-

M.Sc. Hala Ayad M. Rasheed

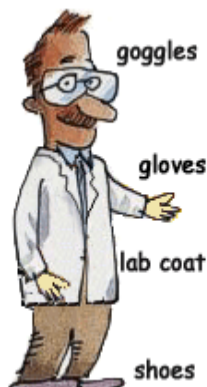
M.Sc. Hawazin Aziz Hamim



1. Always wash your hands before and after experiments. (bring small towel and a bar of soap with you)
2. Read all directions for the experiment carefully before beginning. Follow all the directions exactly as written or explained by the supervisor.
3. Never perform unauthorized activities.
4. Never mix chemicals or other materials for fun.
5. Maintain a clean work area.
6. When an experiment is completed always clean up the glass ware and working area and return all equipment's to its proper place.
7. Never eat in lab (DO NOT CHEW GUM)



8. Know the location of safety equipment's (e.g. Fire extinguisher) and how to use it.
9. Always wear safety goggles when working with chemicals, burners, or any substance or object that might injure eyes.
10. Wear your lab. coats as soon as you enter the lab. and keep it on the whole time. (student NOT ALLOWED to enter the lab unless he has his coat on)



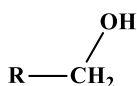
11. Keep all lids closed immediately when a chemical is not being used.
12. Many chemicals and hazardous materials might be corrosive or even poisonous. never touch, taste, or smell any chemical. If instructed to smell the fumes in an experiment, gently wave a hand over the opening of the container and direct the fumes toward the nose.
13. Dispose of all chemicals as instructed by the supervisor.
14. Take care not to spill any chemicals on your bench or in the lab. If spilling does occur, notify the supervisor for clean-up directions.
15. Be careful if you work with acids and bases. Always pour acid into water gradually when diluting the acid. NEVER pour water into acid.
16. Rinse any acids or bases off skin or clothing with water.
17. Never reach across a flame.
18. Pull back long hair and push up long sleeves if necessary.
19. Always point a test tube or bottle being heated away from you and others.
20. Never heat chemicals in a closed container.
21. Always use a clamp, tong, or heat-resistant gloves when handling with hot containers.
22. Use a wire screen to protect glassware when heating.
23. Never heat glassware that is not thoroughly dry.
24. Never use broken or chipped glassware. If glassware break notifies the supervisor.
25. Notify the supervisor immediately if you are cut or injured in lab. (For first aid)
26. All sharp glass ware and broken glass are to be disposed of in the proper container. (Notify the supervisor)



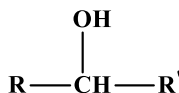
EXPERIMENT 1

IDENTIFICATION OF ALCOHOL COMPOUNDS

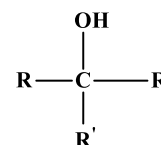
- Alcohols are compounds contain hydroxyl groups (OH) attached to carbon atoms (alkyl group = R). Suffix (-ol) used in the molecule of a hydroxyl group.
- Alcohols divided into three types:
 - Primary alcohol:** - (-OH) are attached to carbon atom that attached to one carbon atom.
 - Secondary alcohol:** - (-OH) are attached to carbon atom that attached to two carbon atoms.
 - Tertiary alcohol:** - (-OH) are attached to carbon atom that attached to three carbon atoms.



1° alcohol



2° alcohol



3° alcohol

- Some of alcohol compounds: - ethanol, methanol, isopropanol, tert-butanol, cyclohexanol.

Physical properties:

Colorless liquid, have characteristic odor, miscible in water, toxic, burned by blue flame.

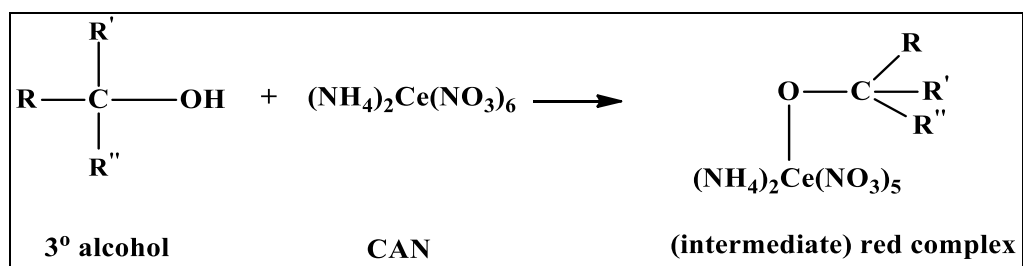
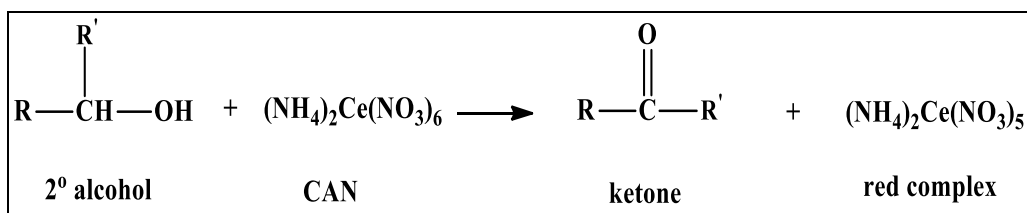
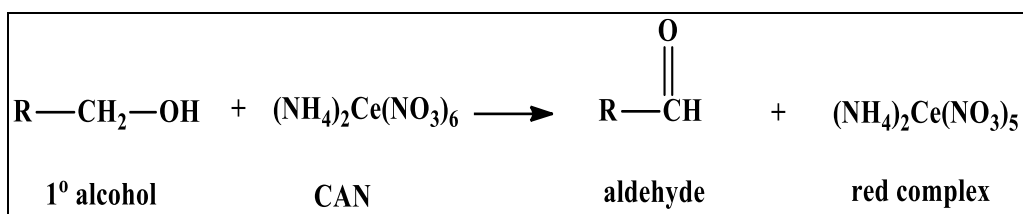


Chemical properties:

1. The effect of the compound on the litmus paper: - They are neutral compounds because they don't change the color of litmus paper.

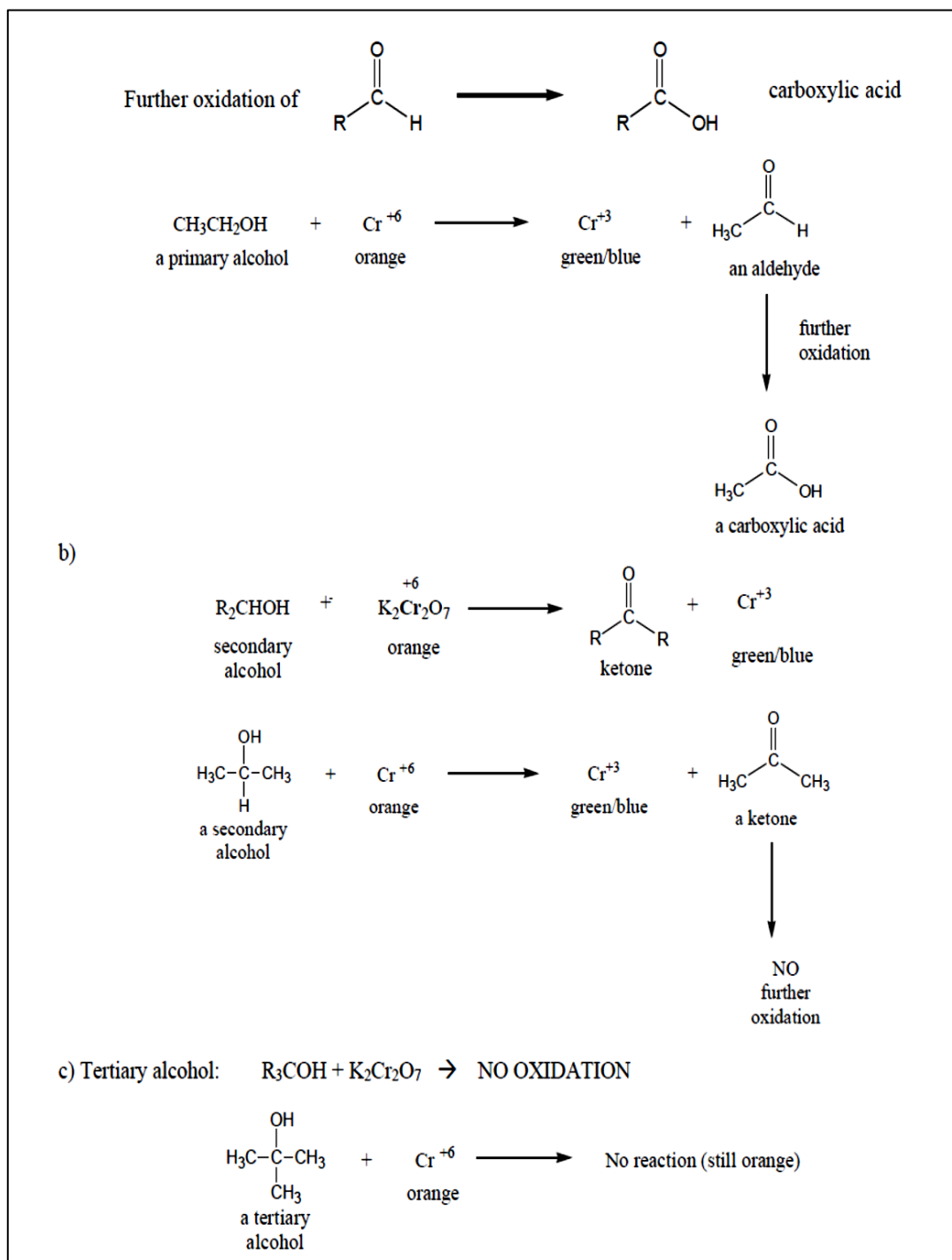
2. General test by (ceric ammonium nitrate test):

(CAN) oxidizing agent that oxidized alcohol compounds to give positive result (red complex) by oxidation –reduction reaction. Phenol compounds give negative result brown to greenish brown precipitate while other functional group give yellow color.



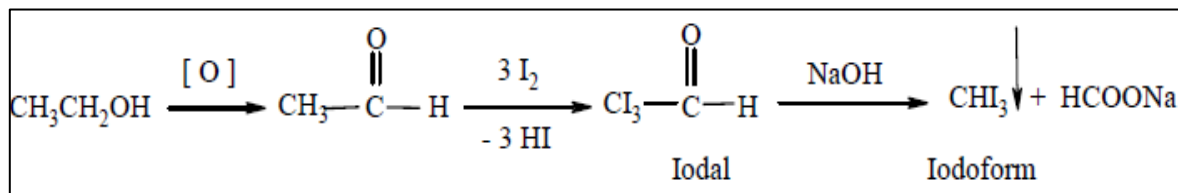
3. Oxidation test:

It was found that Primary alcohols oxidize to aldehyde while the Secondary alcohols oxidizing to ketone, but tertiary alcohols not oxidized when used strong oxidants such as $\text{K}_2\text{Cr}_2\text{O}_7$ in H_2SO_4 is according to the following equations.



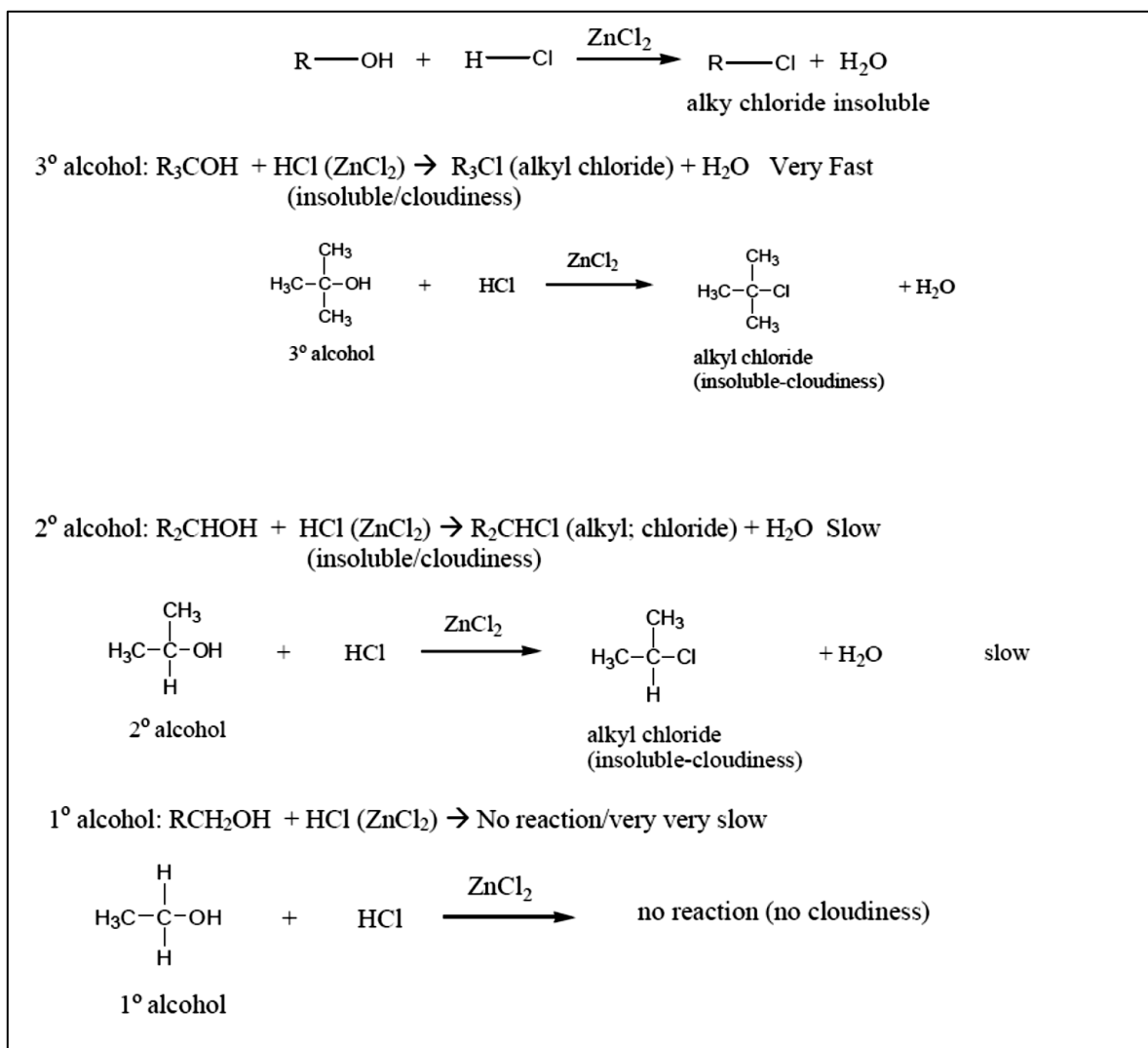
4. Iodoforms Test:

This test is specific for terminal CH_3 group of alcohols. alcohol oxidized to aldehyde or ketone then addition (I_2) to ($-\text{CH}_3$) to form triiodo derivatives (Iodal) then formation (CHI_3) and carboxylic salt as pale-yellow ppt.



5. The Lucas test:

This test distinguishes among the three types of alcohols (1°, 2°, and 3°), by the speed with which they react. The reaction is a replacement reaction, where a Cl from (con. HCl+ ZnCl₂) replaces the hydroxyl group on the alcohol.





- ✓ 3° alcohols react very fast with the Lucas reagent (HCl mixed with ZnCl_2), and will turn cloudy almost immediately.
- ✓ 2° Secondary alcohols do react, but more slowly and must be heated in a water bath in order to react and turn cloudy.
- ✓ 1° Primary alcohols react so slowly (even in a warm water bath) that NO REACTION is observable. The color will stay the same without any precipitate is a **negative** result.





Alcohols tests Procedure:

1. **Ceric ammonium nitrate:** - In test tube add (4-5) drops of alcohol compounds, dissolved in water if not dissolved added few drops of dioxan. Add (2-4) drops of (CAN) shake the mixture well and observe the result. Positive result is red color.
2. **Oxidation test:** - In a test tube put 1ml of alcohol (ethanol) then 1ml of potassium dichromate $K_2Cr_2O_7$ and drops of conc. H_2SO_4 . The green/blue color is chromium sulphate $Cr_2(SO_4)_3$ which formed due to the oxidation of primary or secondary alcohols.
3. **Iodoform test:** - in a test tube add 4 drops or (0.1g from solid) alcohol to 1ml of H_2O (if immiscible with water add 5ml of dioxin) then 3ml of iodine solution & heat in water bath for 3 min. then cool & add 10% NaOH drop wise till the color is pale yellowish ppt of iodoform is produced.
4. **Lucas's test:** - Add to one of alcohol few drops of Lucas reagent (6 drops) shakes well and observed the results: -
 - ✓ 3° alcohols react very fast with the Lucas reagent (HCl mixed with $ZnCl_2$), and will turn cloudy almost immediately.
 - ✓ 2° Secondary alcohols do react, but more slowly and must be heated in a water bath in order to react and turn cloudy.
 - ✓ 1° Primary alcohols react so slowly (even in a warm water bath) that NO REACTION is observable. The color will stay the same without any precipitate is a **negative** result.

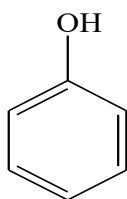


EXPERIMENT 2

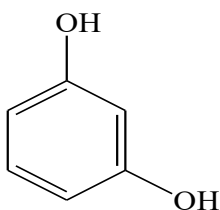
IDENTIFICATION OF PHENOLS COMPOUNDS

Phenol is aromatic compound contains one or more hydroxyl group (OH) connected directly to aromatic nucleus. Phenol classified according to the number of hydroxyls contained group into:

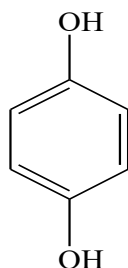
- Monohydric phenol
- Dihydric phenol
- Trihydric phenol



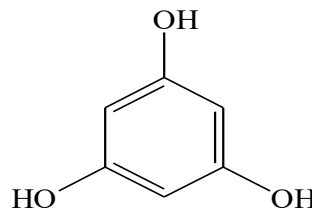
Phenol



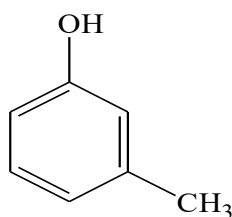
Resorcinol



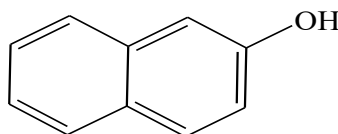
Hydroquinone



Benzen-1,3,5-triol



m-cresol



Naphthalen-2-ol

Physical Properties:

Most phenol is solids in pure state (except m-cresol), which turned to light red when exposed to air it has characteristic odor. Soluble in water, alcohols, ethers, and sodium hydroxide, ignite by yellow smoky flame.

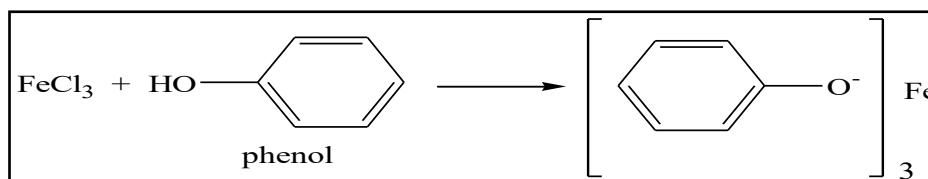


Chemical Properties:

1. Ferric chloride test:

Phenols react with ferric chloride to give colored compounds due to the presence of $[-C=C-OH]$ (enol) group. Indeed, this reaction is considered as a test for any compound with enol group the results:

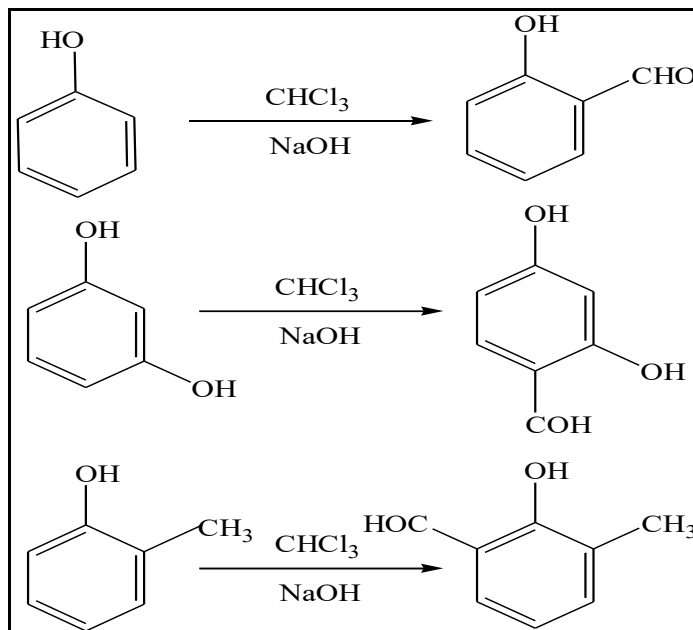
- Violet color $\rightarrow$ phenol or *m*-cresol
- a deep violet color $\rightarrow$ resorcinol
- greenish blue $\rightarrow$ *o*- and *p*-cresol
- deep green $\rightarrow$ Hydroquinone
- no characteristic color $\rightarrow$ β -Naphthol



2. Riemer - Tiemann reaction:

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

- If no color or yellow $\rightarrow$ Phenol
- If a red fluorescent $\rightarrow$ Resorcinol
- If a brown color $\rightarrow$ hydroquinone
- if blue color change to green $\rightarrow$ β -Naphthol
- If a deep orange color $\rightarrow$ *o*-cresol
- If a pale orange color $\rightarrow$ *m*-cresol
- If a yellow color $\rightarrow$ *p*-cresol



Phenols Test Procedure:

- Ferric chloride test:** - few crystals of the solid phenol or few drops dissolved in ethanol then add 2 drops of (5%) ferric chloride solution and observe the resulting color.
- Riemer - Tiemann reaction:** - few amounts of phenol add 1 ml of 30% NaOH solution and 1 ml of chloroform, heat on water bath, and observe the color.

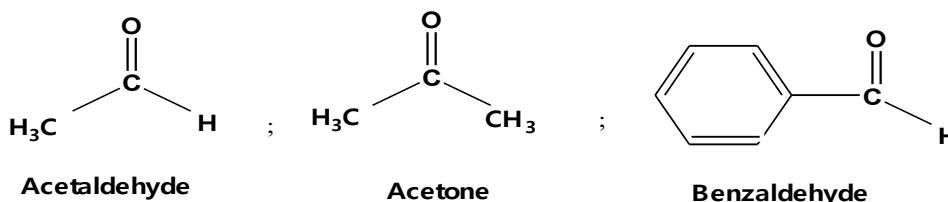


EXPERIMENT 3

IDENTIFICATION OF CARBONYL COMPOUNDS

- Aldehydes are produced by oxidation of primary alcohols.
- Ketones produced from oxidation of secondary alcohols.

Examples:



Physical Properties:

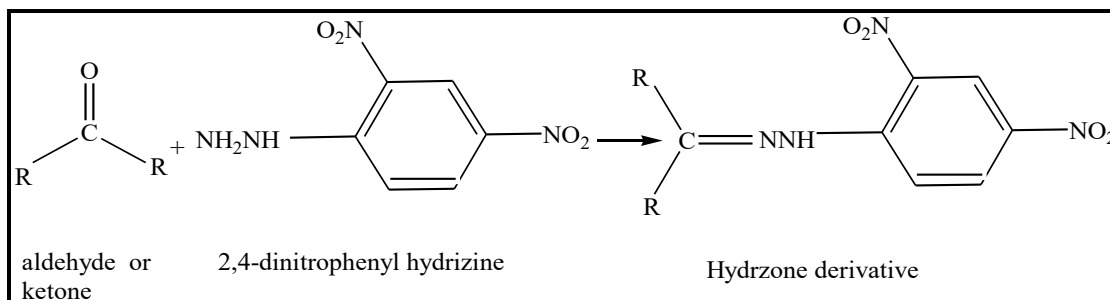
Colorless liquid (except formaldehyde it is gas), have characteristic odor, aliphatic aldehyde and ketone are miscible with water while aromatic aldehyde and ketone are immiscible with water.

Chemical Properties:

1. The effect of the compound on the litmus paper: - Aldehydes and ketones are neutral compounds and not change the color of litmus paper.

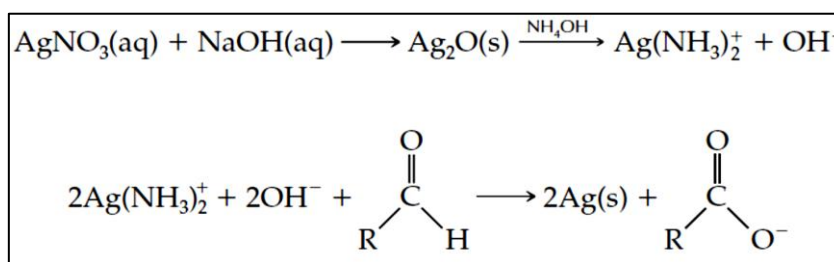
2. General test for aldehydes and ketones (2,4-dinitrophenylhydrazine)

Aldehydes and ketones react with a hydrazine derivative through nucleophilic addition and subsequent loss of water to give yellow or orange precipitate of hydrazone derivative. The reagents that are often used for this purpose are 2,4-dinitrophenylhydrazine.



3. Tollens' Test

Tollen's reagent is the combination of silver nitrate solution with ammonium hydroxide in the presence of sodium hydroxide solution. This reagent gives a silver mirror in the presence of aldehydes because the reaction between them involves the oxidation of the aldehyde to the corresponding carboxylic acid with an accompanying reduction of silver ion from this reagent to silver element in the form of a silver mirror.

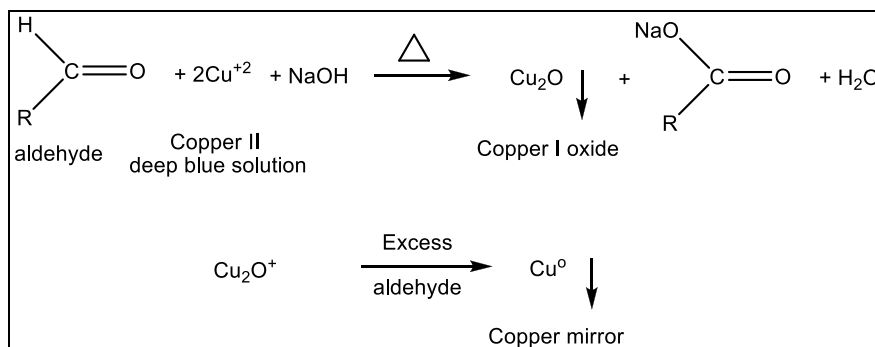


The oxidation process needs alkaline medium; therefore, sodium hydroxide solution is used, and in order to overcome the formation of the brown silver oxide precipitate (Ag_2O), ammonium hydroxide is used to serve as a complexing agent for this precipitate making it a water-soluble complex.

Note that since the medium is alkaline, salts of the produced carboxylic acid are formed rather than the acid itself.

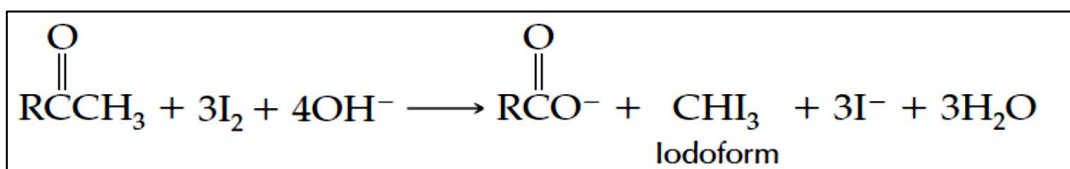
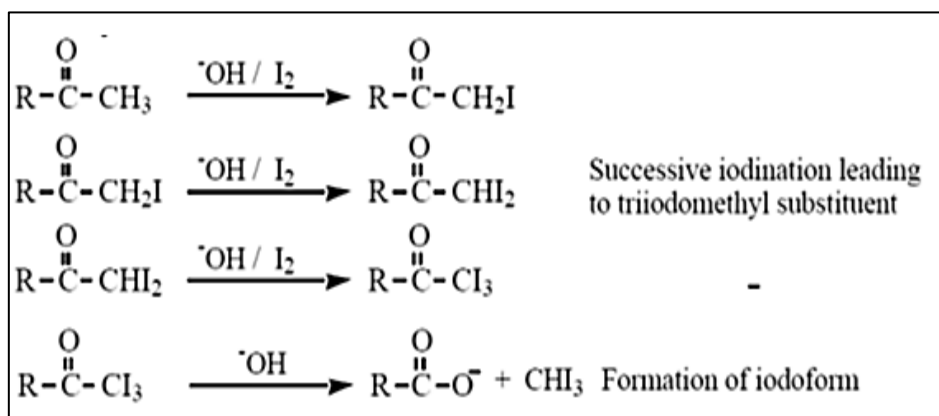
4. Fehling test

This test, like Tollen's test, is used to distinguish aldehydes from ketones. Only aldehydes can reduce Fehling's reagent (a deep blue solution) to give a red cuprous oxide precipitate (Cu_2O).



5. Iodoform test: -

It is specific for aldehydes and ketones that contain ($-\overset{\text{O}}{\underset{\text{||}}{\text{C}}}-$) group. (I_2) add ($-\text{CH}_3$) to form triiodo derivatives (Iodal) then formation (CHI_3) and carboxylic salt as pale-yellow ppt.





Carbonyl Test Procedure:

- 3. General test:-** If compounds miscible with water added 2 drops of compound. If compounds immiscible with water add methanol or ethanol then 1ml H₂O and 3ml of 2,4-dinitrophenylhydrazine. The color of the hydrazone precipitate formed is a yellow or orange ppt is an indication of the presence of carbonyl group.
- 4. Tollen test:** - add (4-5) drops of carbonyl compounds that have terminal CH₃, add (2-4) drops of (AgNO₃ \ NH₄OH) solution, shake the mixture well then added (2 drops) of (NaOH 10%) shake the mixture well and observe the result. Positive result is silver mirror that mean (aldehyde only).
- 5. Fehling test:** - Add 5 drops of the compound to 1 ml of Fehling's solution, and then heat in water bath for 5 minutes (with shaking for water insoluble compounds). Aldehydes change the color of Fehling's solution from blue to green, orange precipitate, and then red precipitate or copper mirror. Ketones don't change the color of this reagent.
- 6. Iodoform test:** - In test tube add (4-5) drops of carbonyl compounds. Add (1ml) of (I₂ \ KI) solution, shake the mixture well red color result. Heat the mixture for (10-15min) on water bath then cool and dissolved in NaOH 10%. Positive result is yellow ppt that mean (CHI₃).



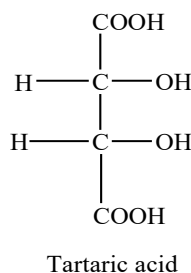
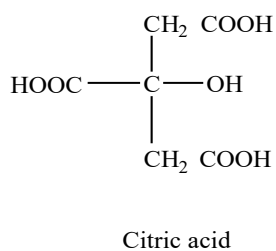
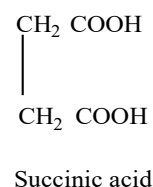
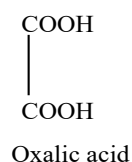
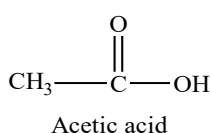
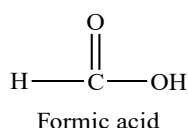
EXPERIMENT 4

IDENTIFICATION OF CARBOXYLIC ACID COMPOUNDS

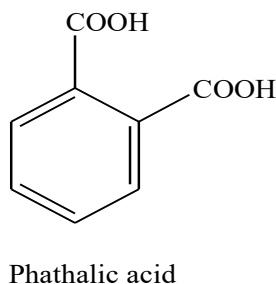
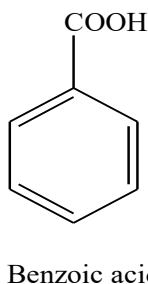
- All acids contain carboxyl group COOH.

Also, Aliphatic and aromatic acid can divide into different types according to number of carboxylic groups in the molecules or according to type or number of another group attached to acid molecules: -

✚ Aliphatic acids:



✚ Aromatic acid:





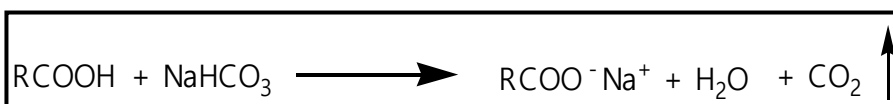
Physical Properties:

1. Colorless solids (except formic acid, acetic acid and lactic acid which are liquids).
2. The boiling points & melting point of carboxylic acid are higher than those of alcohols of similar size because the carboxylic acid can form hydrogen bonds with each other as well as van der Waals dispersion forces and dipole-dipole interactions.
3. Aliphatic carboxylic acids are soluble in water. However, solubility decreases rapidly with increase of carboxylic acid molecules. This is because the longer hydrocarbon chain of acid molecules tends to break hydrogen bonds. Also soluble in sodium hydroxide, sodium bicarbonate.

Chemical Properties:

1. **The effect of the compound on the litmus paper:** - Carboxylic acids turn litmus paper blue to red.
2. **general test by sodium bicarbonate:** -

When a carboxylic acid reacts with sodium bicarbonate (NaHCO_3), it produces a carboxylate salt, water, and carbon dioxide gas, resulting in a brisk. This reaction is a common test to identify the presence of a carboxylic acid group in a molecule.

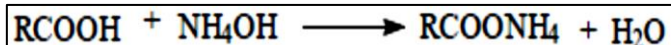


3. **Ferric chloride test:** -

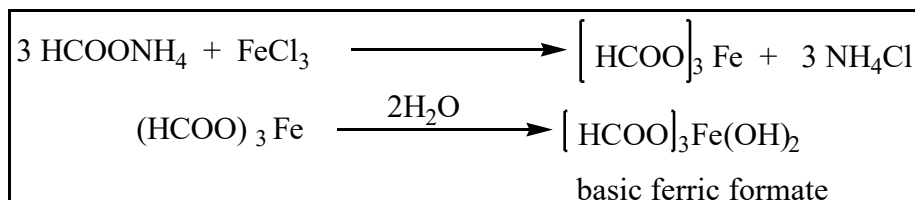
The acid solution should be made neutral before performing the test with ferric chloride solution. N.S (neutral solution) of acid with ferric chloride solution gives specific color for each acid.



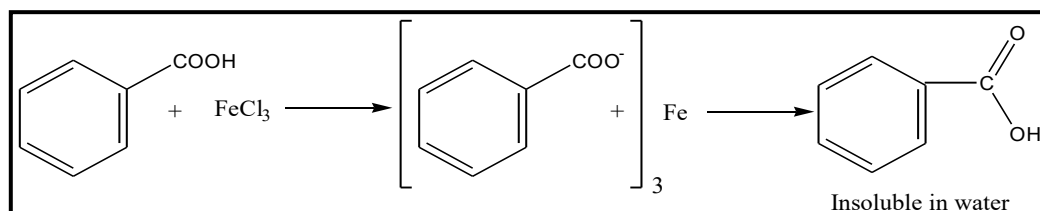
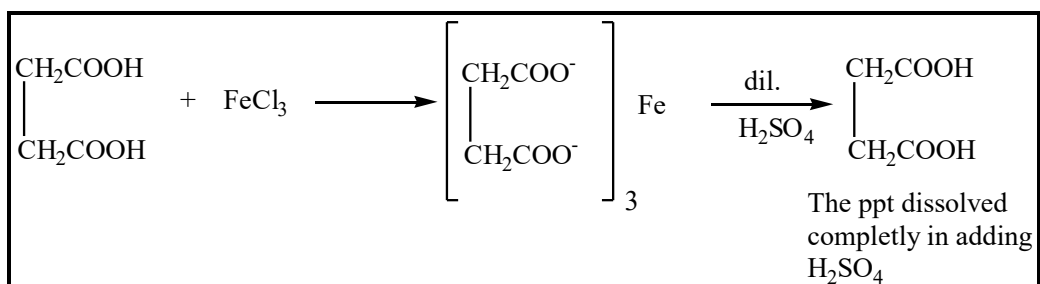
Neutral Solution of acid:



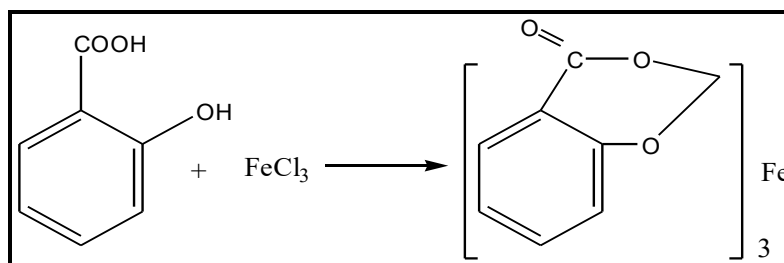
a. If a dark red ppt. → Indicate the presence of acetate salts or formate salt.



b. If pale brown ppt. → indicate the presence of succinic acid or benzoic acid.



c. If violet color → indicates the presence of salts of salicylic acid.

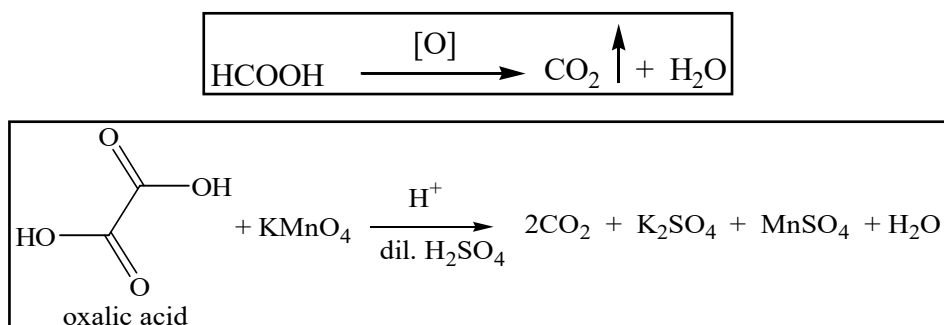


d. And if no color change than the acid is oxalic or citric or tartaric or lactic acid.



4. Alkaline Permanganate test:

Formic acid or oxalic acid reacts with potassium permanganate solution, a strong oxidizing agent, in alkaline medium causing decolorization of the reagent.

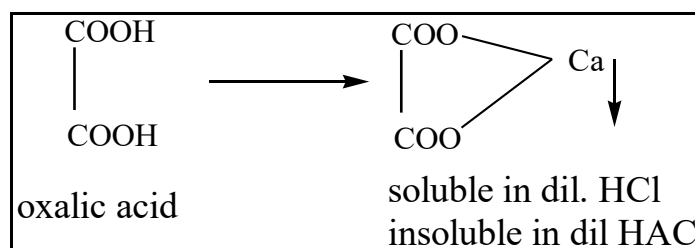


- a. But if the color will not disappear → indicate the presence of acetic acid.

5. Calcium chloride test:

Tartaric acid or oxalic acid reacts with calcium chloride solution, neutral acid (salt of acid) reacts with reagent to produced specific white ppt for each acid.

- a. If a white ppt. will appear on cold → indicate the presence of oxalic acid (The ppt. is calcium oxalate specific test for oxalic acid).



- b. But if a white ppt. appears after scratching the inner wall of the tube → indicate the presence of tartaric acid (The ppt. is calcium tartrate specific test for tartaric acid).



Carboxylic acid Test Procedure:

- 1. General test:** - Few amounts of compound then (1ml) of sodium bicarbonate (NaHCO_3). Observed result
- 2. Ferric chloride test:** - adding dilute ammonia solution drop by drop with shaking to a solution of about 0.5 gm of the acid in water until the medium becomes basic as indicated by changing the color of litmus paper to blue to obtain neutral solution acid. Cool the solution, and then add few drops of ferric chloride solution to get different colors of solutions or precipitates
- 3. Alkaline Permanganate test:** - Mix 2 - 3 drops of the acid with 5 ml of sodium bicarbonate solution, and then add 1% potassium permanganate solution drop by drop and observe the result.
- 4. Calcium chloride test:** - To the neutral solution of the acid (see the general test) add few drops of calcium chloride solution. Observed the result.



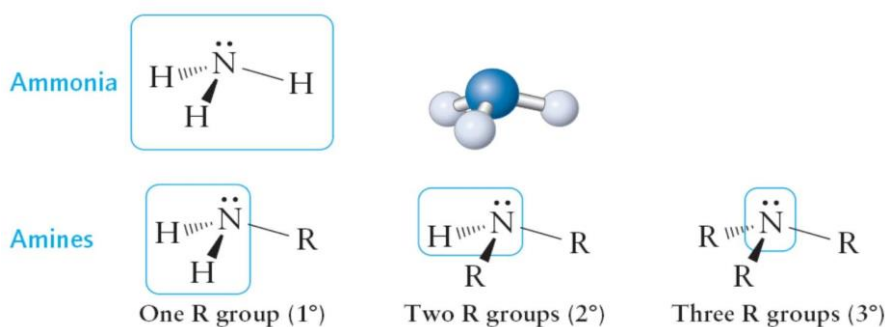


EXPERIMENT 5

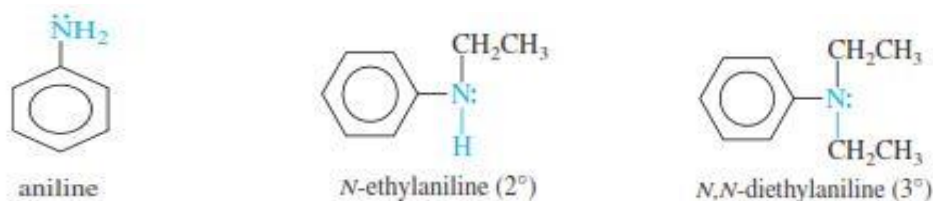
IDENTIFICATION OF AMINES COMPOUNDS

Amine is organic compounds derived from ammonia. Aliphatic amine when alkyl groups bonded to (N) atom. Aromatic amine when aryl group bonded to (N) atom. Amines classified according to one or two or three alkyl or aryl group bonded to (N atom) into:

- Primary and Secondary and Tertiary aliphatic amine.



- Primary and Secondary and Tertiary aromatic amine.



Physical Properties:

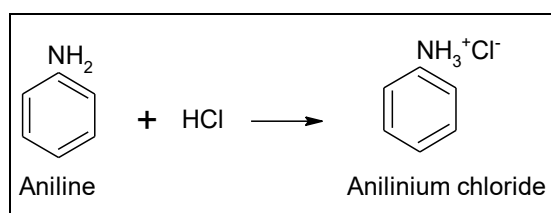
Amines are solids or liquid. It has characteristic odor like fish. It was soluble in water and HCl dil. because amines are basic compounds. Most of amine's compounds are carcinogenic.



Chemical Properties:

1. General test (The hydrochloric acid test): -

Amines are characterized chiefly through their basicity. Amine was soluble in water when have less (5 carbon) atom turn litmus red into blue while insoluble in water when amine have more than (5 carbon) atom so that dissolves in dilute hydrochloric acid.



2. Nitrous acid test:

It is test for distinguish between (1°, 2°, 3°) amine but it is specific for aromatic amine for distinguish.

- ❖ Nitrous acid is unstable and must be prepared immediately by mixing sodium nitrite (NaNO₂) with acid (HCl dil).



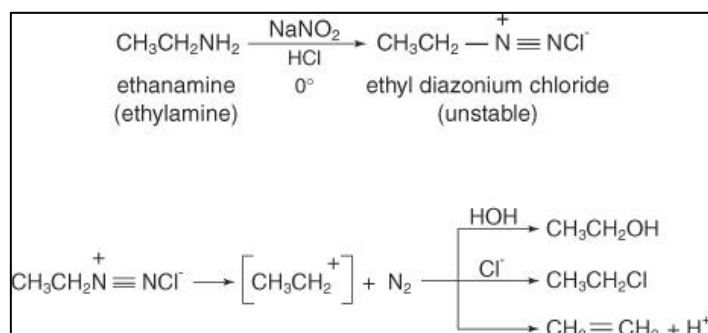
- **Primary amine:** - give diazonium salt clear solution, so coupling with phenol compounds to give azo-dye if used aromatic amine while aliphatic amine gives clear solution and N₂ gas because the diazonium salt of aliphatic amine unstable.
- **Diazonium salts:** Diazonium compounds or diazonium salts are a group of organic compounds with the general molecular structure R-N₂⁺ X⁻, where R may



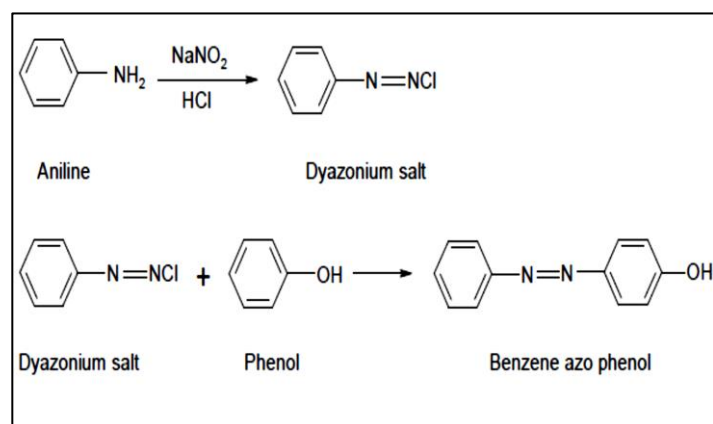
be any alkyl or aryl group and X may be halogens, hydrogen sulphate etc. Aryl diazonium salts have frequently been used as intermediates in organic synthesis.

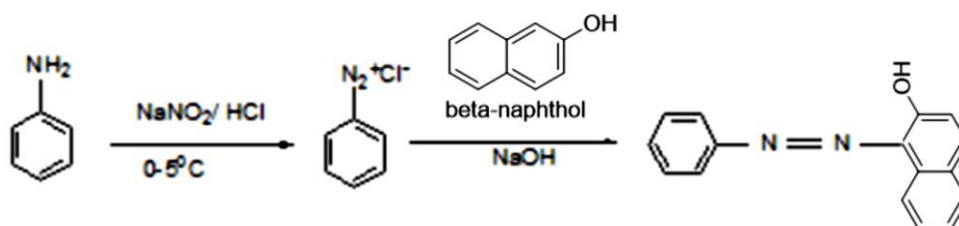
- **Coupling reactions:** Coupling reactions are those in which diazonium salts are linked or coupled with another molecule such as phenols. The whole reactions are commonly called azo coupling. Diazonium salts being weak electrophiles, as a consequence they react with those aromatic systems which are activated by strong electron donating groups. It is for this reason diazonium salts usually undergo coupling reactions with phenols and aromatic amines in alkaline, neutral or mild acidic medium to yield highly colored azo compounds.

1° aliphatic amine: -

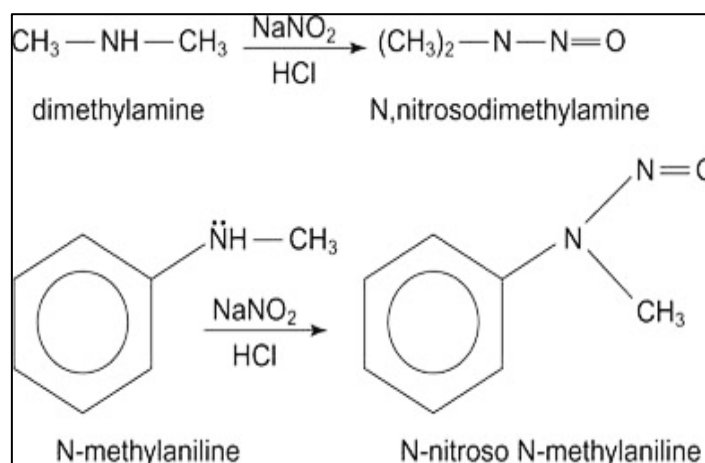


1° aromatic amine: -

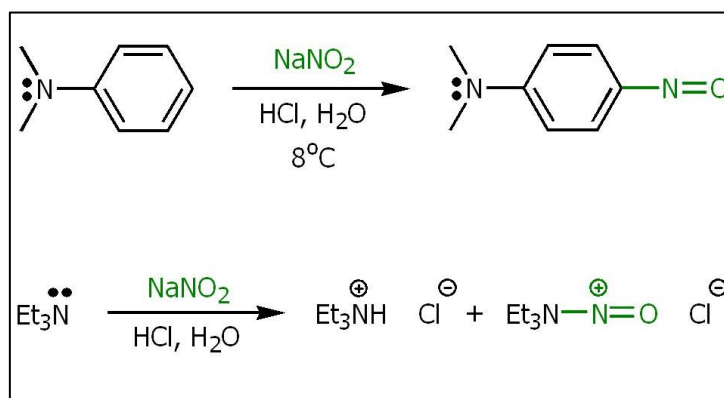




- **Secondary amine:** - give yellow oil layer (form nitrosoamine).



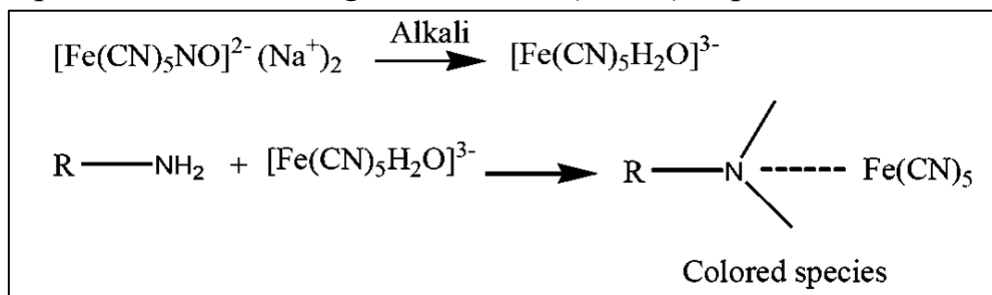
- **Tertiary amine:** - give green or red precipitate that's aromatic while give clear solution its aliphatic (N-nitrosoammonium compounds).





3. Sodium nitroprusside test (SNP test): -

It is specific test for distinguish between (1, 2, 3) aliphatic amine.



- 1° aliphatic amine observed violet color.
- 2° aliphatic amine observed blue color.
- 3° aliphatic amine no color

Amine Test Procedure:

1. General test (The hydrochloric acid test): - in a clean test tube, mix 3 ml of water then 2 drops or few amounts of amine. If compound is soluble, test the pH of the solution by litmus paper. If compound is not soluble in water, add 3 ml of HCl 5% solution. If compound dissolves in the acid solution, an amine is indicated.

2. Nitrous acid test: - Take 2 test tubes.

Tube (1): 0.5ml of amine + 1.5 ml of HCl (10%).

Tube (2): 1ml of solution of sodium nitrite NaNO_2 (20%).

Keep test tubes in ice bath and add tube (2) to tube (1) slowly, and observe result:



- If give yellow oil layer (form nitrosamine) that's mean **secondary amine**.
- If give green or red precipitate that's **tertiary aromatic**.
- while give clear solution its **primary amine** so applies **coupling reaction**.
- **Coupling reaction** for primary amine. Take new test tube: 0.1g β -Naphthol dissolved in 2ml of 10% NaOH. This solution added to the mixture of the above tube and observed results: -
 - If a red dye color $\rightarrow$ Phenol, Resorcinol
 - If an orange-red ppt. $\rightarrow$ β -Naphthol

3. Sodium nitroprusside test (SNP test): - 1ml of amine and 0.5 ml of acetone then 0.5ml of water and 2 drop f (SNP) solution then shake observed color.

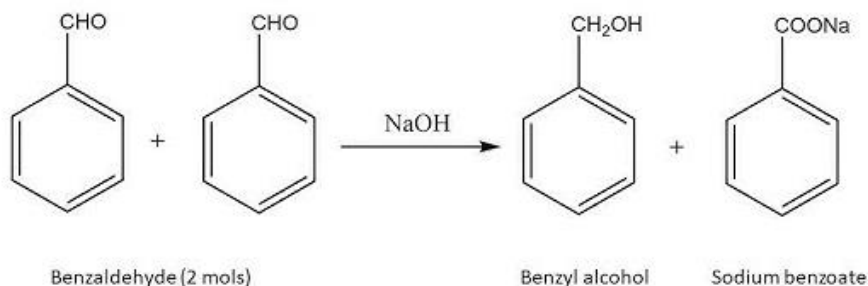




EXPERIMENT 6

CANIZZARO REACTION

One of the notable organic reactions in chemistry is the Cannizzaro reaction, named after its discoverer, Stanislao Cannizzaro. The Cannizzaro reaction is a redox reaction where an aldehyde (without α -hydrogens) is converted into a carboxylic acid and a primary alcohol when treated with a strong base. In this disproportionation reaction, one molecule of the aldehyde is oxidized to a carboxylic acid salt, while another is reduced to an alcohol. Examples include formaldehyde, which yields methanol and formic acid, and benzaldehyde, which forms benzyl alcohol and benzoic acid.

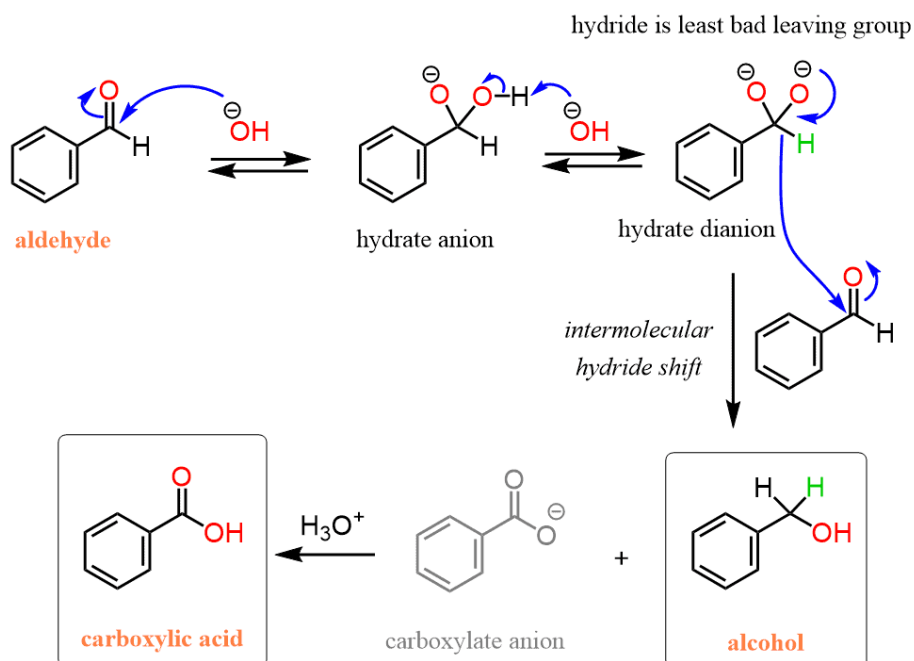


This mechanism of the experiment performed: -

First step:- A hydroxide ion from the strong base performs a nucleophilic attack on the aldehyde's carbonyl carbon.

Second step: - A hydride ion (H^-) is then transferred from one aldehyde molecule to another.

Third step:- the molecule that loses the hydride is oxidized to a carboxylic acid salt, and the molecule that gains the hydride is reduced to an alcohol.



Safety Note: -

- During addition of nitrating mixture, the temperature of the reaction mixture should not rise above 10°C.
- Addition of fuming nitric acid should be done drop wise.
- Addition of nitrating mixture may preferably be done in a fume-cupboard.

Procedure:

Experimental: Chemicals: Glacial acetic acid (GAA), Acetanilide, Con. H₂SO₄, Con. HNO₃

Add (0.7g) of powdered acetanilide in round bottom flask (100mL). Add (0.7ml) of glacial acetic acid and stir the mixture by the use of glass-rod. Carefully add drop by drop (0.7ml) of con. sulphuric acid with constant shaking and cooling. Add (0.5ml) of fuming nitric acid in a clean test-tube and cool it in ice bath then add (0.5ml) of con. H₂SO₄ drop by drop in cooling condition.



Add slowly the solution of the tube to round flask containing acetanilide and glacial acetic acid. Place the flask in a ice bath for 10 minutes. Remove the flask from the ice bath and allow it to stand for 30 minutes at room temperature. Pour the contents of the flask on the crushed ice taken in a beaker. Stir it and filter the crude product. Wash the solid on the filter paper with cold water to remove acid. Dry the solid, weigh it and record its yield. Recrystallization of p-nitro acetanilide with hot ethanol.