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| College of Pharmacy | الكلية |
| Pharmaceutical Chemistry | القسم |
| Pharmaceutical Organic Chemistry II | المادة باللغة الانجليزية |
| الكيمياء العضوية الصيدلانية | المادة باللغة العربية |
| Fourth grade | المرحلة الدراسية |
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| Preparation of Nitrobenzene | عنوان المحاضرة باللغة الانجليزية |
| تحضير النايتروبنزين | عنوان المحاضرة باللغة العربية |
| 6 | رقم المحاضرة |
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محتوى المحاضرة

Nitrobenzene (C₆H₅NO₂)

1-Introduction

Nitrobenzene is an important aromatic nitro compound.

Industrially valuable as a precursor to aniline.

Highly toxic and environmentally hazardous.

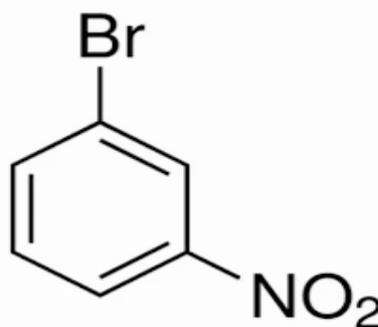
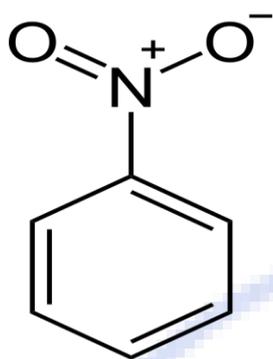
It is a compound that contains a nitro group (NO₂-), which can be attached to a carbon atom (as in nitrobenzene)

2-Structure

Molecular formula: C₆H₅NO₂

Benzene ring with an –NO₂ substituent.

Nitro group is electron-withdrawing → meta-directing.



3-Physical Properties

Molecular formula: $C_6H_5NO_2$

Molar mass: 123.11 g/mol

Density: 1.199 g/cm³

Boiling point: 210 °C

Melting point: 5.7 °C

Oily pale yellow liquid (colorless when pure).

Slightly soluble in water; miscible with alcohol, ether, benzene.

Odor: Almond-like (toxic at low levels).

4- Chemical Properties

1. General properties

Electrophilic substitution: Ring is deactivated, meta-directing.

Reduction: Nitrobenzene → Aniline (Sn/HCl or Fe/HCl).

Further nitration → Di-/Tri-nitrobenzene (explosives).

It contains a nitro group (-NO₂) attached directly to the benzene ring.

The nitro group is strongly electron-withdrawing (electron-withdrawing), making the aromatic ring less reactive in aromatic substitution reactions.

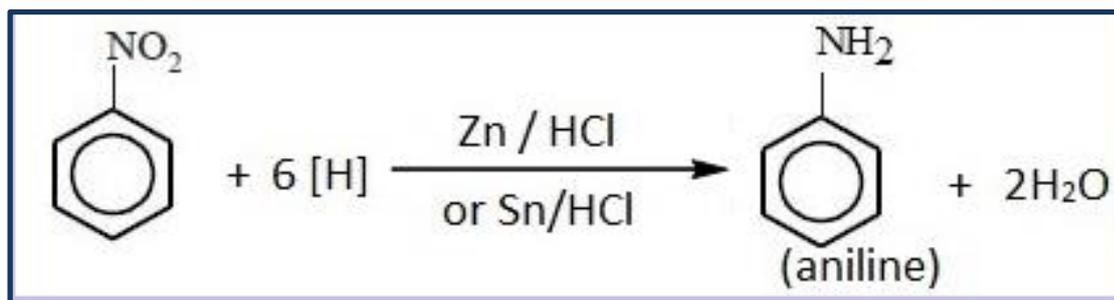
Therefore, reactions on the ring are slow and tend to occur in meta-directing positions.

2- Reduction of nitrobenzene in different medium :

Nitrobenzene gives different products in different medium by using different reducing agent.

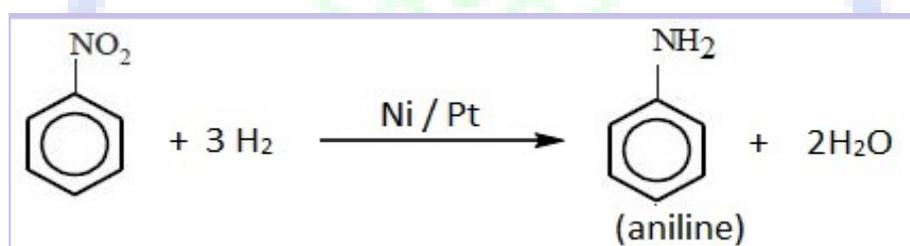
Reduction of nitrobenzene in acidic medium :

Nitrobenzene on reduction with Zn/HCl or Sn/ HCl gives aniline



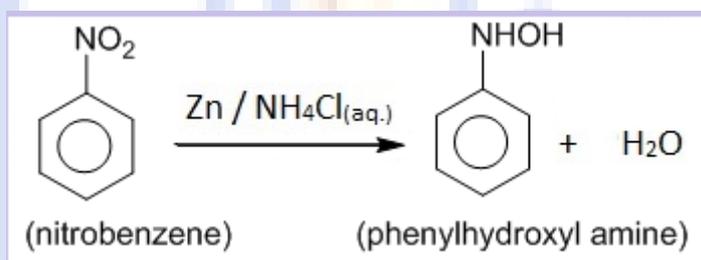
Catalytic reduction of nitrobenzene :

Nitrobenzene when reduced by hydrogen in presence of nickel or platinum as a catalyst gives aniline.



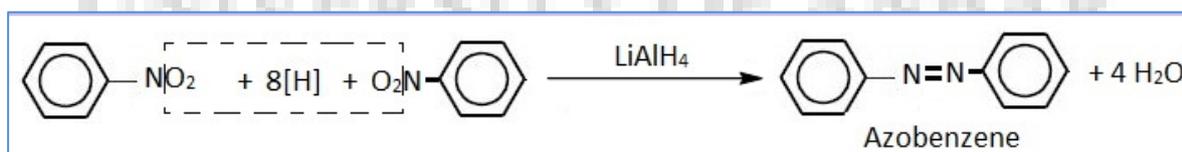
Reduction of nitrobenzene in neutral medium :

Nitrobenzene on reduction with Zn and aq. NH_4Cl gives phenyl hydroxylamine.



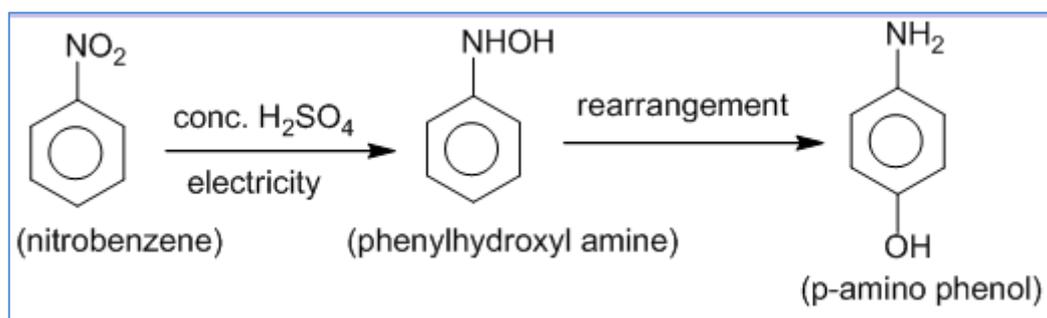
Reduction of nitrobenzene with LiAlH_4 :

Lithium aluminium hydride reduces nitrobenzene to azobenzene.

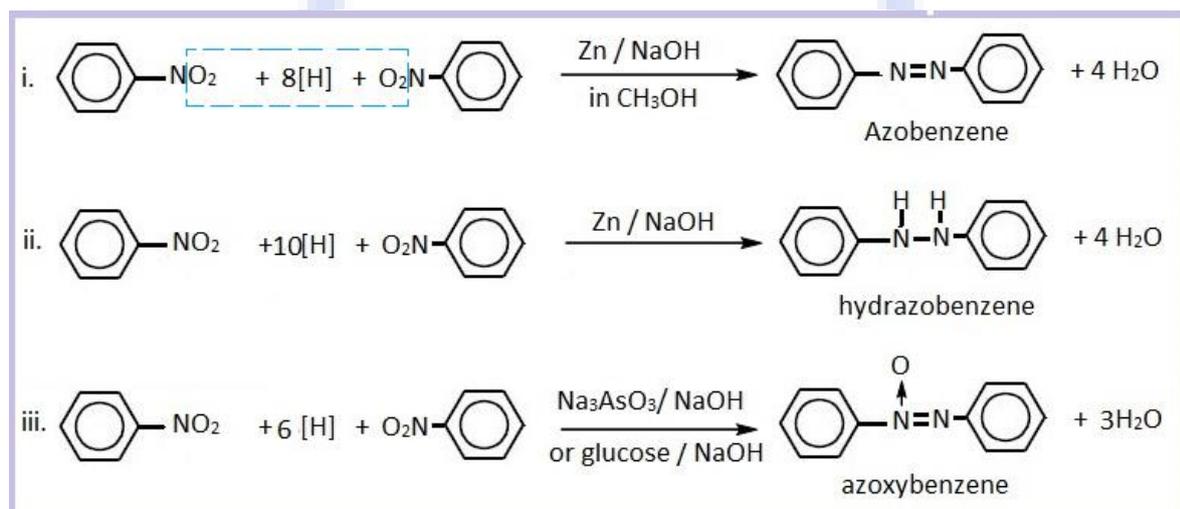


Electrolytic reduction of nitrobenzene :

Nitrobenzene when reduced electrolytically, first gives phenyl hydroxylamine which immediately rearranges to give p-aminophenol.



Reduction of nitrobenzene in alkaline (basic) medium :



3-Reactions of nitrobenzene due to benzene ring :

NO₂ group is electron withdrawing group. It withdraws π - electrons from benzene ring, decreasing electron density of aromatic ring.

Nitrobenzene is resonance hybrid of following resonance structures

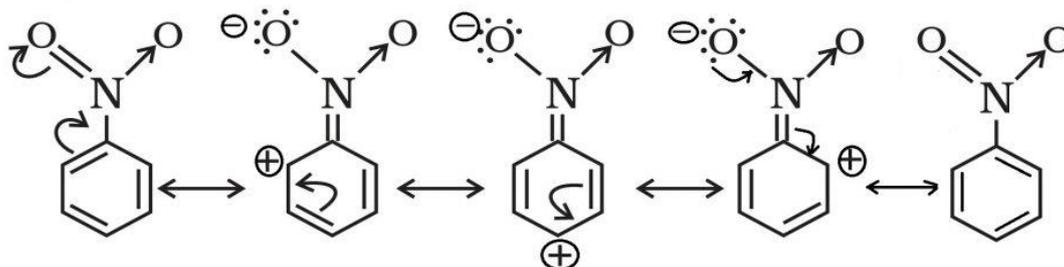
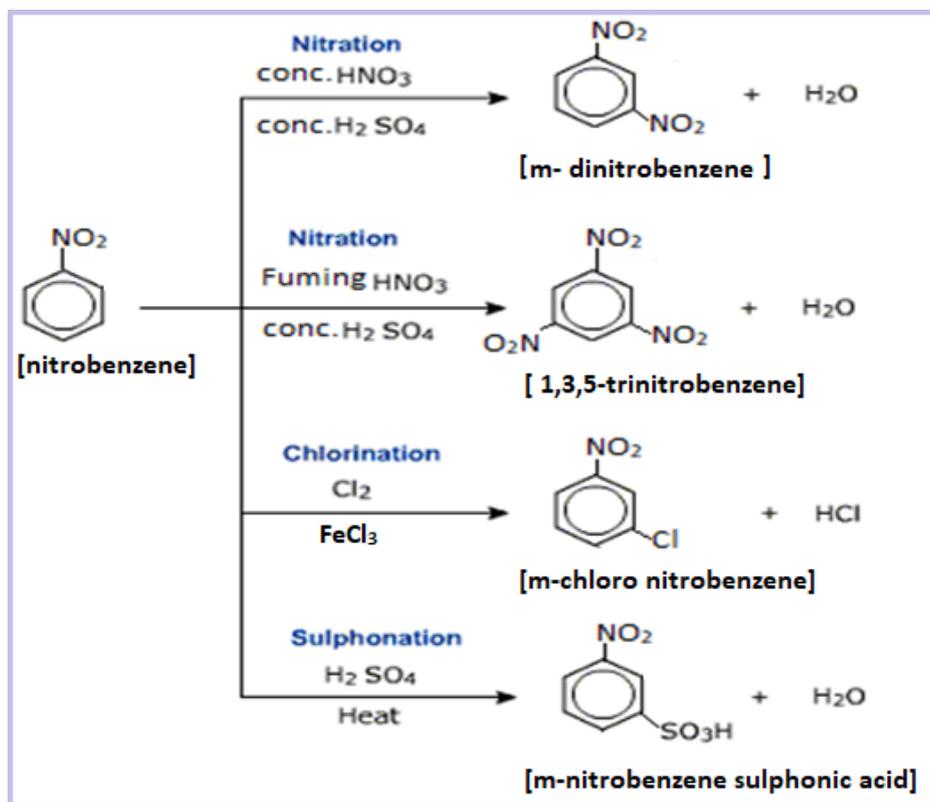


Fig. Resonance structures of nitrobenzene.

4-Electrophilic substitution reactions of nitrobenzene



5- Reactions with Strong Bases

Under harsh conditions (heat + strong base), it can decompose or react via base-reduction mechanisms.

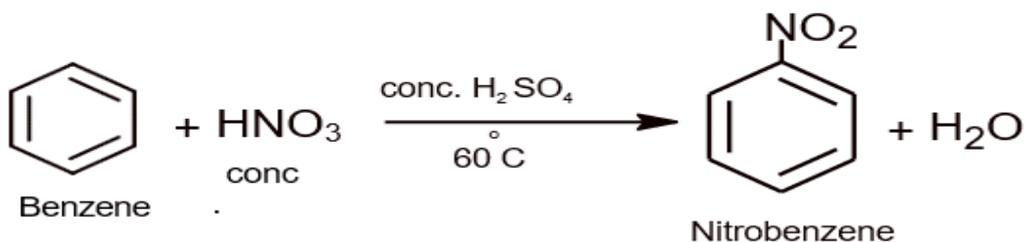
6. Stability

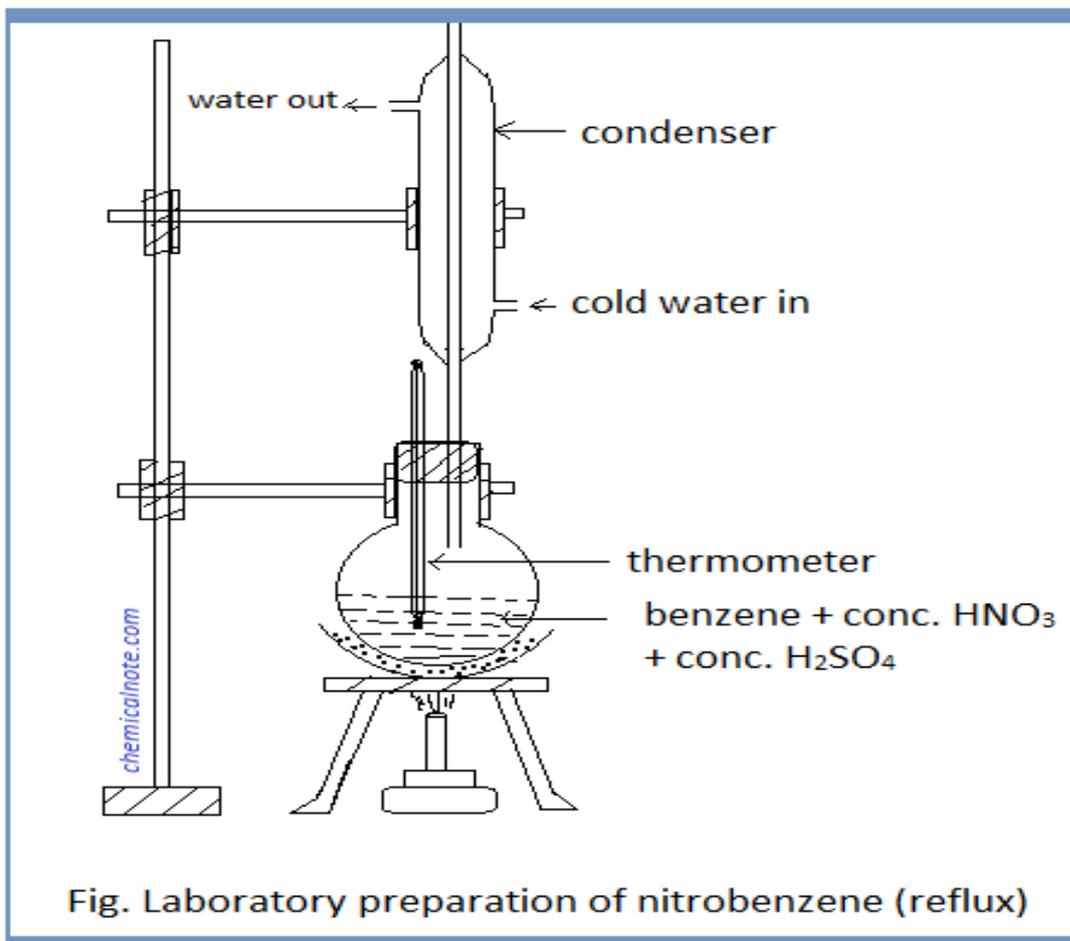
Nitrobenzene is relatively thermally stable, but it can participate in strong oxidation reactions, producing compounds such as CO_2 and NO_x .

5- Preparation

- ▶ **Industrial method:** Nitrobenzene is prepared by nitrating benzene using a concentrated mixture of sulfuric acid and nitric acid.
- ▶ **Benzene + $\text{HNO}_3 \rightarrow$ Nitrobenzene + H_2O (catalyzed by H_2SO_4).**
- ▶ **Conditions: 50–60 °C.**

Modern processes: Continuous reactors, safer nitrating agents





Purification :

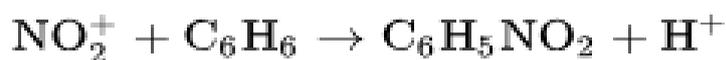
It is first washed with dil. Na_2CO_3 to remove the acidic impurities and then with water several times. It is then dried over fused calcium chloride. It is finally distilled at 211°C to get pure nitrobenzene

6- Mechanism

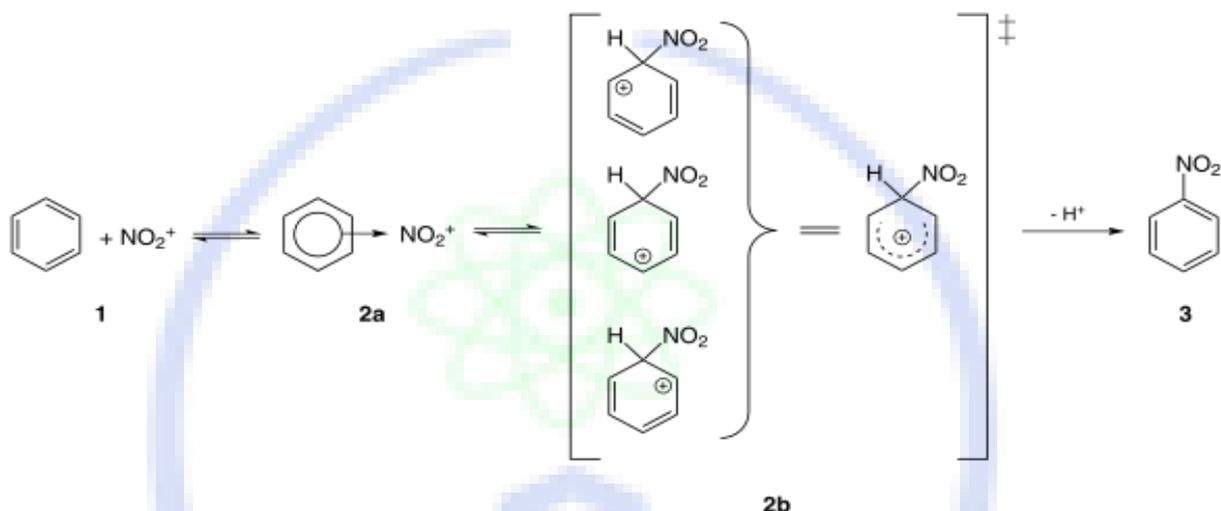
- ▶ A mixture of sulfuric acid and nitric acid reacts to form the nitronium ion NO_2^+ (or nitrile ion):



- ▶ The chemically active nitronium ion reacts with benzene by an electron-loving aromatic substitution mechanism to form nitrobenzene:

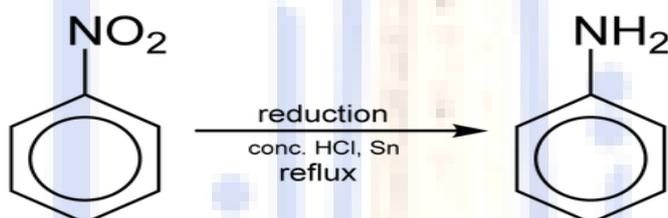


- ▶ The preparation of nitrobenzene is one of the most dangerous preparation reactions in the chemical industry, as the reaction is highly exothermic ($\Delta H = -117 \text{ kJ/mol}$).



7- Applications

- ▶ %95 used for aniline production.



- ▶ Aniline derivatives \rightarrow dyes, rubber chemicals, pharmaceuticals.
- ▶ Precursor to TNT (explosives).
- ▶ Limited use as solvent due to toxicity.

8- Toxicity & Health Effects

- ▶ Absorbed by inhalation, ingestion, skin contact.
- ▶ Converts hemoglobin \rightarrow Methemoglobin (reduces oxygen transport.)
- ▶ Acute: Headache, dizziness, cyanosis, respiratory distress.
- ▶ Chronic: Anemia, liver and nervous system damage.

- ▶ Carcinogenicity: IARC Group 2B.

9- Environmental Impact

- ▶ Persistent in soil and water.
- ▶ Toxic to aquatic life.
- ▶ Strict disposal and emission regulations.

10- Safety Precautions

- ▶ Use fume hood, gloves, goggles, protective clothing.
- ▶ Continuous air monitoring in industries.
- ▶ Proper waste management.

11-Preparation of Nitrobenzene

- 1 .Slowly add 10 ml of sulfuric acid with 10 ml of nitric acid and 3 ml of distilled water at a temperature of 5°C (3-4 minutes.)
- 2 .Add 10 ml of benzene to mixture (1) in an ice bath (add slowly).
- 3 .Place the mixture in a water bath at 60°C for 30 minutes.
- 4 .Cool the mixture for 5 minutes.
5. Add the mixture to 30 ml of cold distilled water.