

ORGANIC CHEMISTRY

Topic-9

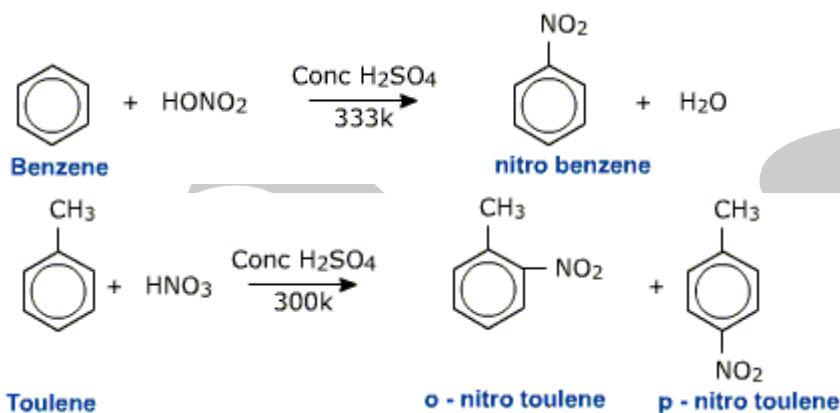
NITROBENZENE

LONG ANSWER QUESTIONS

1. Explain the methods of preparation of Nitrobenzene.

Laboratory preparation of nitrobenzene

Aromatic compounds can be directly nitrated using a mixture of concentrated nitric acid and sulphuric acid.



This reaction is an example of electrophilic substitution of benzene. The electrophile is a nitronium (NO_2^+) ion.

The nitronium ion attacks to the benzene ring resulting in the formation of a carbocation. Electron releasing substituents like $-\text{CH}_3$, $-\text{OCH}_3$, $-\text{OH}$, $-\text{NH}_2$ etc activate the ring and stabilize the carbocation while electron withdrawing groups like $-\text{NO}_2$, $-\text{CN}$, $-\text{SO}_3\text{H}$, $-\text{X}$ deactivate the carbocation.

The nitrating mixture of conc. H_2SO_4 and conc. HNO_3 can nitrate even deactivated compounds like nitrobenzene under refluxing conditions to get m-dinitrobenzene. For nitration of activated aromatic systems like phenol and then ether derivatives, even milder conditions can be used.

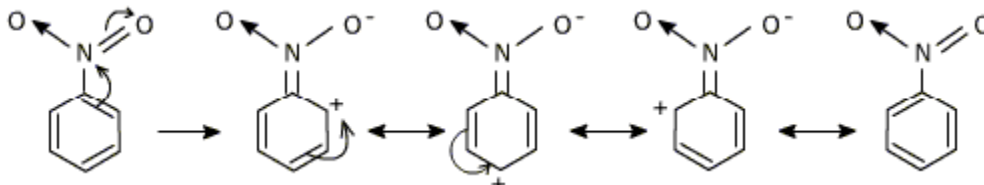
2. Explain the physical and chemical properties of Nitrobenzene.

I. Physical properties of Nitrobenzene:

- Nitrobenzene is a colourless to pale yellow oily liquid that presents a fire hazard.
- Its odour resembles that of bitter almonds or "shoe polish," with odour.
- It is insoluble in water and soluble in organic solvents.

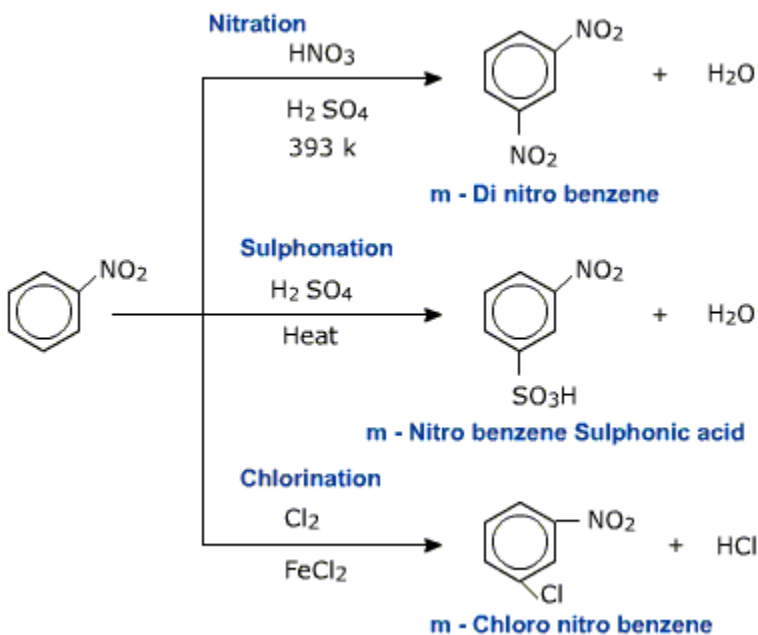
II. Chemical properties of aromatic nitrocompounds

The nitro group strongly deactivates the benzene ring towards electrophilic substitution. Nitro group is electron withdrawing group and thus causes electron deficiency at ortho and para positions as is clear from the resonating structures of nitro benzene.



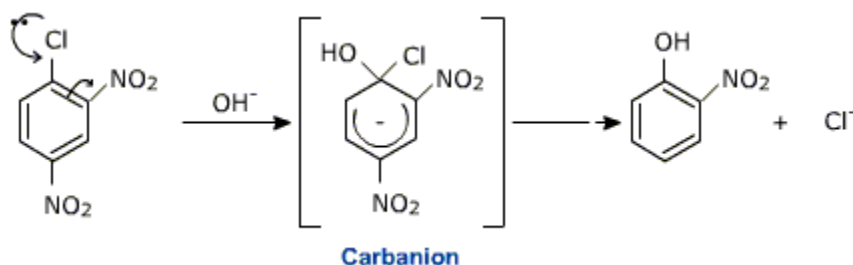
Since the meta position is relatively rich in electron density compared to ortho and para positions electrophilic attack is more likely to occur at meta position. Thus the -NO_2 group is meta directing as far as electrophilic ring substitution is concerned.

A) Electrophilic substitution reaction



b) Influence on the reaction of other functional group

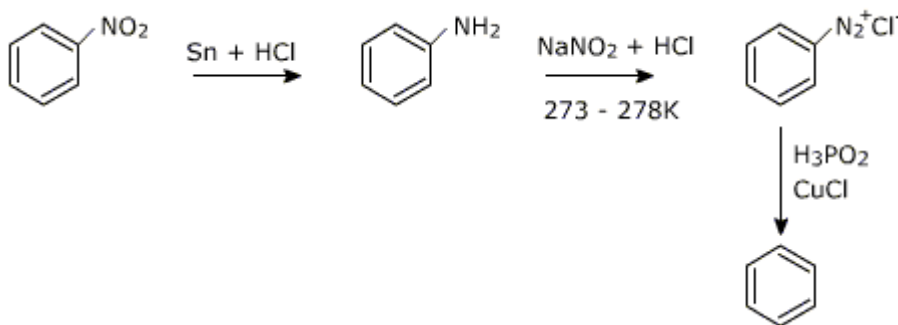
The presence of nitro group facilitates nucleophilic substitution of otherwise unreactive aromatic halides by stabilizing the intermediate carbanion.



c) Reduction of nitrobenzene

The nitro group can be removed from an aromatic ring via the following steps:

- i) Reduction of nitro group to amine
- ii) Diazotization of amine with HNO_2
- iii) Reductive removal of the diazonium group using sodium borohydride or hypophosphorus acid/ Cu^+ mixture.



3. Explain the uses and safety precautions of Nitrobenzene

1 Uses of nitrobenzene

- Approximately 95% of nitrobenzene is consumed in the production of aniline
- More specialized applications include the use of nitrobenzene as a precursor to rubber chemicals, pesticides, dyes, explosives, and pharmaceuticals.
- Nitrobenzene is also used in shoe and floor polishes, leather dressings, paint solvents, and other materials to mask unpleasant odors.
- Redistilled, as oil of mirbane, nitrobenzene has been used as an inexpensive perfume for soaps.
- A significant merchant market for nitrobenzene is its use in the production of the analgesic paracetamol (also known as acetaminophen) (Mannsville 1991)
- Nitrobenzene is also used in Kerr cells, as it has an unusually large Kerr constant.
- Aside from its conversion to aniline, nitrobenzene is readily converted to related derivatives such as azobenzene, nitrosobenzene, and phenyl hydroxylamine. The nitro- group is deactivating, thus substitution tends to occur at the *meta*-position.

2. Safety

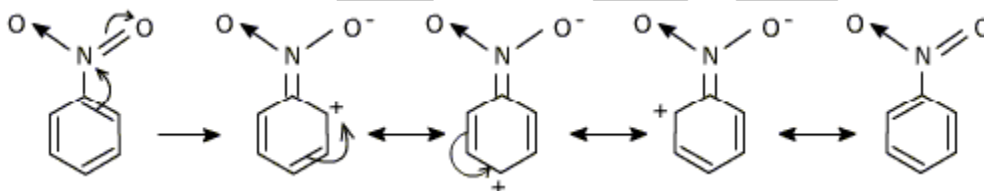
- Nitrobenzene is highly toxic ($\text{TLV } 5 \text{ mg/m}^3$) and readily absorbed through the skin.

- Although nitrobenzene is not currently known to be a carcinogen, prolonged exposure may cause serious damage to the central nervous system, impair vision, cause liver or kidney damage, anemia and lung irritation.
- Inhalation of fumes may induce headache, nausea, fatigue, dizziness, cyanosis, weakness in the arms and legs, and in rare cases may be fatal.
- The oil is readily absorbed through the skin and may increase heart rate, cause convulsions or rarely death.
- Ingestion may similarly cause headaches, dizziness, nausea, vomiting and gastrointestinal irritation.

SHORT ANSWER QUESTIONS

1. Explain the structure of nitrobenzene.

The nitro group strongly deactivates the benzene ring towards electrophilic substitution. Nitro group is electron withdrawing group and thus causes electron deficiency at ortho and para positions as is clear from the resonating structures of nitro benzene.



Since the meta position is relatively rich in electron density compared to ortho and para positions electrophilic attack is more likely to occur at meta position. Thus the $-\text{NO}_2$ group is meta directing as far as electrophilic ring substitution is concerned.

2. Give uses of nitrobenzene.

- More specialized applications include the use of nitrobenzene as a precursor to rubber chemicals, pesticides, dyes, explosives, and pharmaceuticals.
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