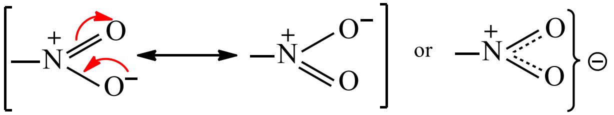
Aromatic nitro compounds

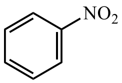
Ref. books:

1. A text book of Organic Chemistry
   - B. S. Bahl and Arun Bahl
2. A text book of Organic Chemistry
   - K. S. Tewari, S. N. Mherotra

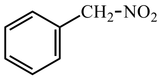
Nitro group structure (–NO_2)



- Nitrocompounds are the derivatives of hydrocarbons which contain one or several groups (–NO_2) in their molecule.
- In modern perspective, aromatic nitro compounds are molecules in which –NO_2 group is directly bonded to an aromatic ring.



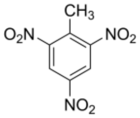
nitrobenzene



phenylnitromethane

Background

- The simplest aromatic nitro compound, **nitrobenzene**, also known as **nitrobenzol**, molecular formula $C_6H_5NO_2$.
- Often highly explosive, especially when the compound contains more than one nitro group.
- One of the most common *explosophores* (functional group that makes a compound explosive) used globally.
- Trinitrotoluene, best known as a useful explosive material with convenient handling properties.



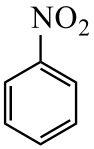
Nomenclature

- Name the longest and continuous carbon chain
- Name the –NO_2 compound as a –nitro substituent

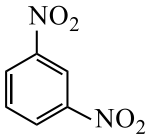
Aliphatic Nitro

$CH_3{-}NO_2$

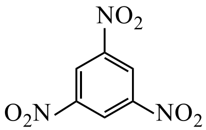
Nitromethane



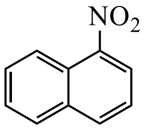
Nitrobenzene



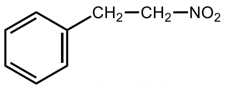
m-dinitrobenzene
1,3-dinitrobenzene



1,3,5-trinitrobenzene



1-nitronaphthalene

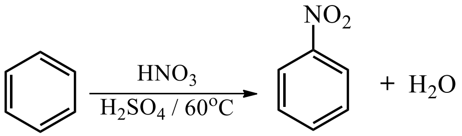


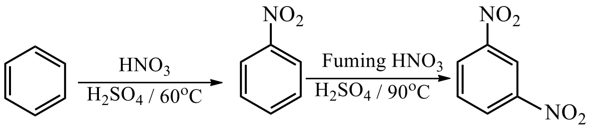
1-nitro-2-phenylethane

Preparation

Direct nitration

Nitrobenzene is prepared by nitration of benzene with a mixture of concentrated sulfuric acid, water, and nitric acid, called "mixed acid."

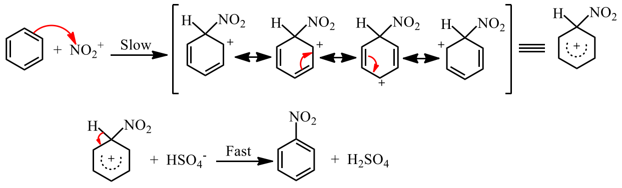




Mechanism of nitration

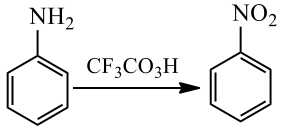
- ❖ The reaction pathway entails formation of an adduct between the Lewis acidic nitronium ion, NO_2^+, and benzene.
- ❖ The nitronium ion is generated in situ via the reaction of nitric acid and an acidic dehydration agent, typically sulfuric acid.

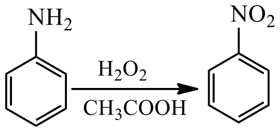
$$HONO_2 + 2H_2SO_4 \rightleftharpoons NO_2^+ + H_3O^+ + 2HSO_4^-$$



Oxidation of arylamines

Arylamines undergo oxidation with trifluoroperacetic acid or hydrogen peroxide in acetic acid to give the corresponding aromatic nitro compounds.



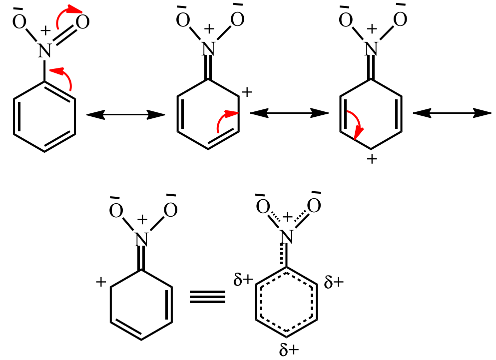


Physical properties of aromatic nitrocompounds

- ❖ Nitrobenzene is a water-insoluble oil which exhibits a pale yellow to yellow-brown coloration in liquid form (at RT and P) with an almond-like odour.
- ❖ When frozen, it appears as a greenish-yellow crystal. Although occasionally used as a flavoring or perfume additive,
- ❖ Nitrobenzene is highly toxic in large quantities and is mainly produced as a precursor to aniline.
- ❖ In the laboratory, it is occasionally used as a solvent, especially for electrophilic reagents.

Chemical properties of aromatic nitro compounds

Resonance hybrid structure of atomatic nitro compounds

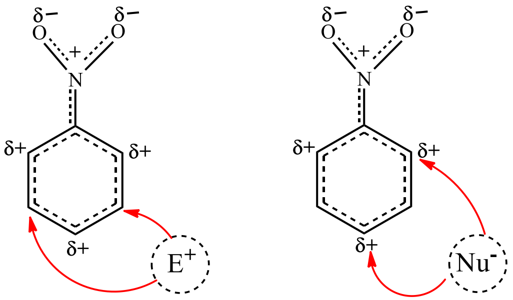


Resonance hybrid

Chemical properties

- C-N bond in hybrid has partial double bond character, $-NO_2$ group is firmly bonded to benzene ring.
- Nitro group ($-NO_2$) cannot ordinarily be replaced by other atoms or groups.
- The benzene ring is deactivated to electrophile (E^+) and activated to nucleophile (Nu^-).

Chemical properties



- Electrophilic substitution occurs with difficulty at relatively election-rich *m*-position.
- Nucleophilic substitution occurs at the o-and p-positions bearing positive charge.

Reactions of nitro compounds

Reactions involving $–NO_2$ group

Reduction of nitro compounds

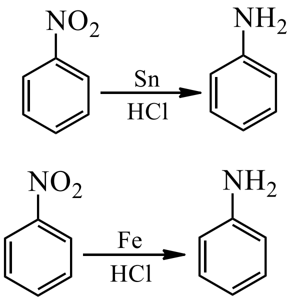
- Aromatic nitro compounds give a variety of products depending on the reagent and conditions (acid, neutral or alkaline medium) used.

$$C_6H_5NO_2 \longrightarrow \underset{\text{Nitrosobenzene}}{C_6H_5NO} \longrightarrow \underset{\text{Phenylhydroxylamine}}{C_6H_5NHOH} \longrightarrow \underset{\text{Aniline}}{C_6H_5NH_2}$$

Reactions of nitro compounds

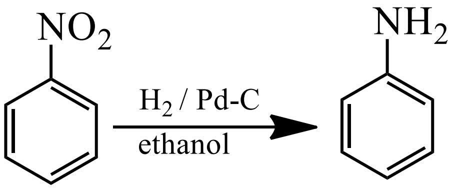
Reduction in acidic medium

(i) By metal in acidic solutions: metals(Fe, Sn and Zn) and HCl are used for reducing a nitro group to an amino group.



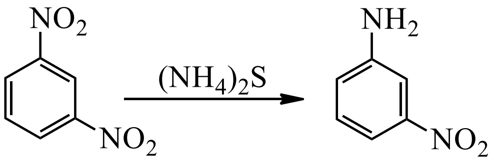
Catalytic reduction

- ❖ The reduction of $-NO_2$ to $-NH_2$ can also be accomplished by catalytic hydrogenation (H_2 in presence of Ni or Pt, or Pd/C.



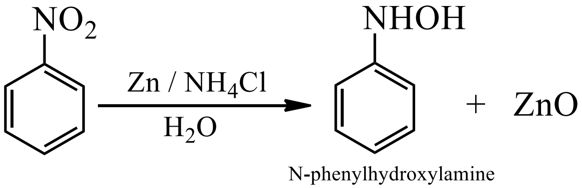
Selective reduction

- ❖ One nitro group can be reduced without affecting the second group on benzene ring using ammonium sulphide or sodium hydrosulphide (NaSH).



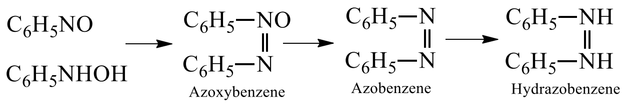
Reduction in neutral medium

(iii) Reduction in neutral medium: zinc dust and ammonium chloride convert nitro benzene to corresponding hydroxylamine.



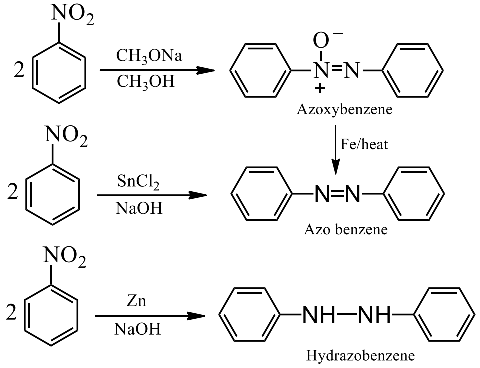
Reduction in alkaline medium

- ❖ On reduction, nitrobenzene forms the mono molecular intermediate products nitrosobenzene and phenylhydroxylamine. In alkaline medium, these undergo bimolecular condensation reactions.



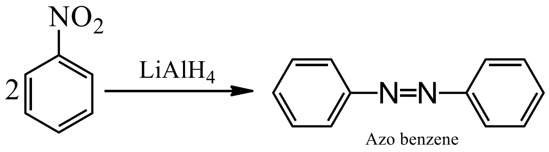
Reduction in alkaline medium

Forms different products depending on reducing reagent.



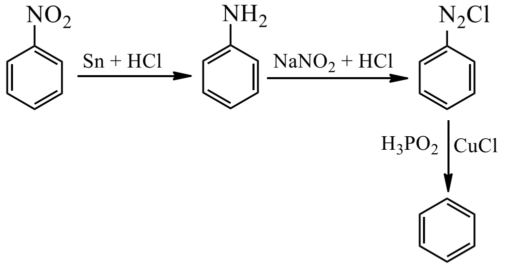
Reduction with $LiAlH_4$

- ❖ Aromatic nitro-comopunds on reduction with $LiAlH_4$ give azo compounds.



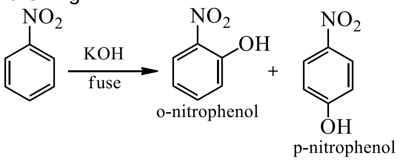
Reductive removal of nitro group

- ❖ Nitro group can be removed from aromatic ring via reduction to amine followed by deoxidization with HNO_2 and then reductive removal of the diazonium group using sodium borohydride or hypo phosphorus acid/Cu^+ mixture.

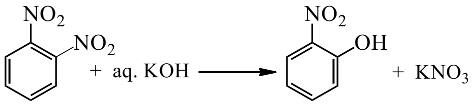


Nucleophilic substitution

- The ortho and para positions of nitrobenzene are attacked by nucleophiles relatively easily. Thus when fused with KOH, nitrobenzene gives o-nitrophenol through necleophilic attack of OH⁻ on the ring.



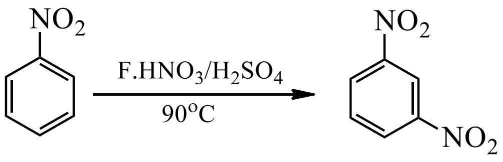
- If a second $-NO_2$ group is present on the benzene ring of nitrobenzene in the ortho or para position, it undergoes nucleophilic displacement.



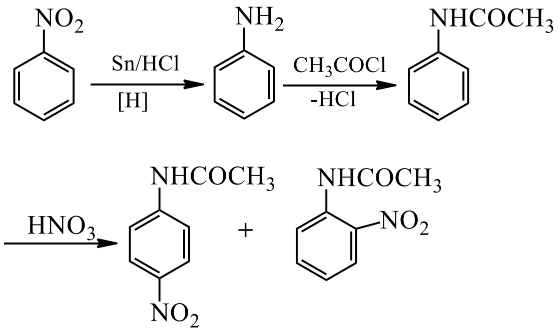
Electrophilic substitution

Nitration: The nitro group strongly deactivates the benzene ring towards electrophilic substitution.

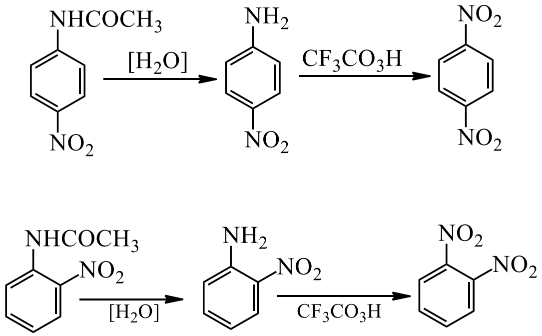
Required strong conditions.



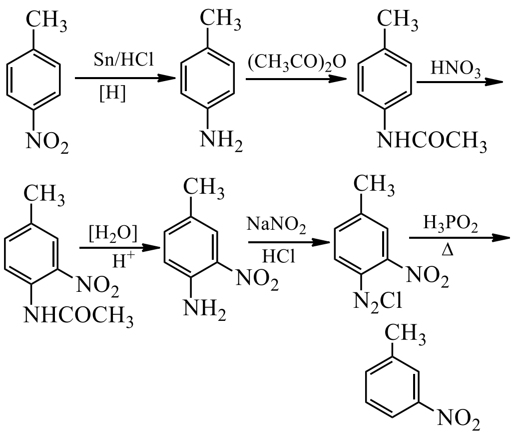
Preparation of o- or p-dinitrobenzene from nitrobenzene



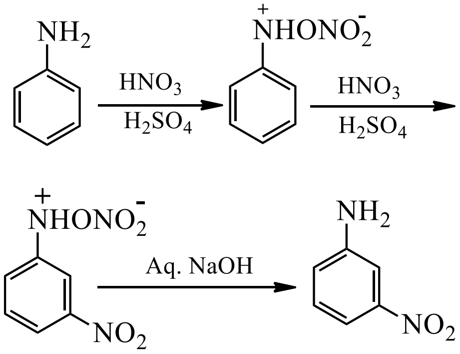
o- and p-nitro acetanilide are separated



Preparation of m-nitrotoluene

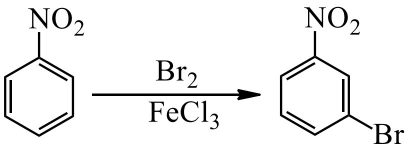


Direct nitration of amine yields some m-nitroaniline

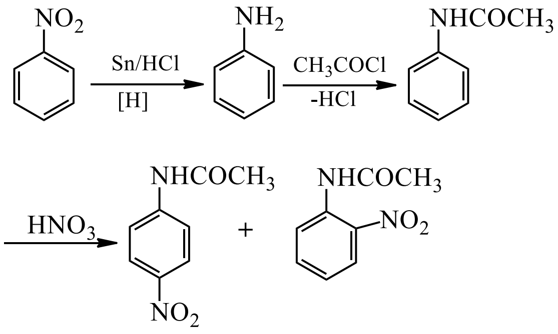


Electrophilic substitution

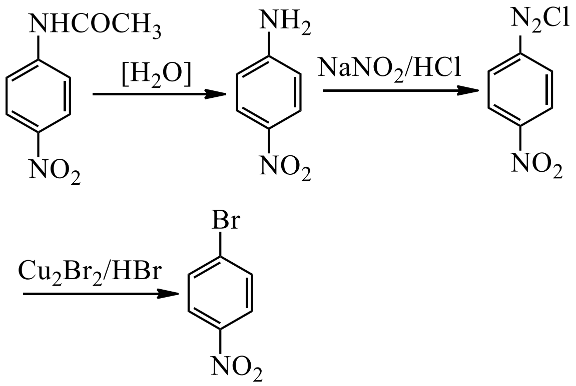
Halogenation: By halogenation nitrobenzene gives m-bromo-nitrobenzene.



Preparation of o- or p-bromo-nitrobenzene from nitrobenzene

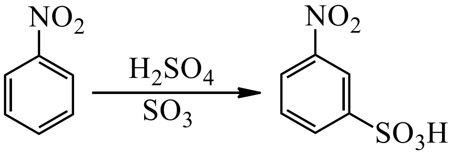


o- and p-nitro acetanilide are separated

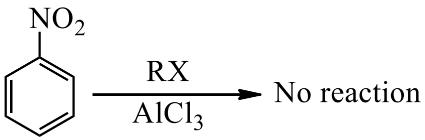


Electrophilic substitution

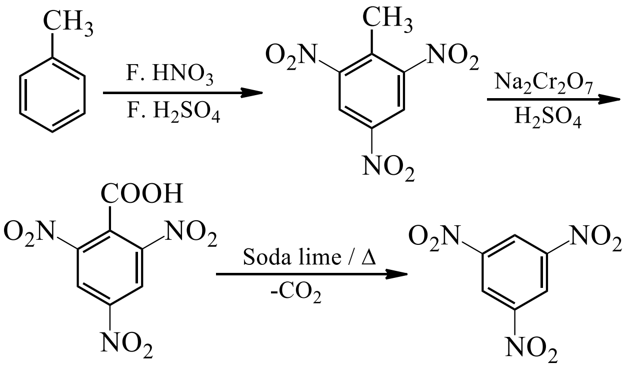
Sulphonation: By sulphonation nitrobenzene yields m-nitro benzenesulphonic acid. For sulphonation fumed sulfuric acid is used



Friedel-Carft alkylation



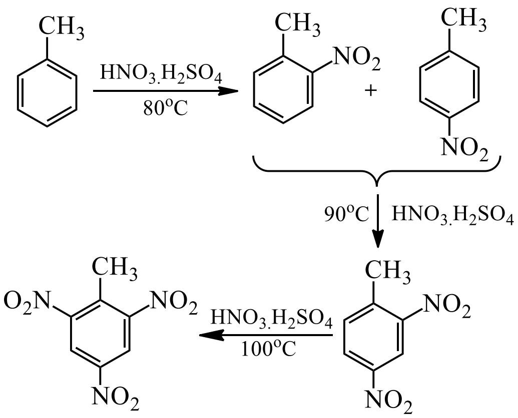
Trinitrobenzene (TNB), $C_6H_5(NO_2)_3$



Properties and uses of trinitrobenzene (TNB)

- It is a colorless solid.
- Melting point 122°C.
- It is more powerful explosive than TNT.
- Because of the difficulty in its preparation, it is not used as explosive.
- It forms well defined crystalline compounds with phenol, hydrocarbons, etc.

Trinitrotoluene (TNT)



Properties and uses of trinitrotoluene (TNT)

- It is a pale yellow crystalline solid.
- Melting point 81°C.
- It is used as an explosive in shells, bombs and torpedoes under the name ‘trotyl’
- ‘Amatol’ (contains 80% ammonium nitrate), is used in mining, especially coal-mining.
- ‘Ammonal’ (contains 47% aluminium nitrate, 22%, aluminium, 30% TNT, 1% charcoal) used for outdoor blasting work