Study Material: 5

Name- Sayanwita Panja

Discipline- B.Sc (H)

Subject- Chemistry

Semester- IV

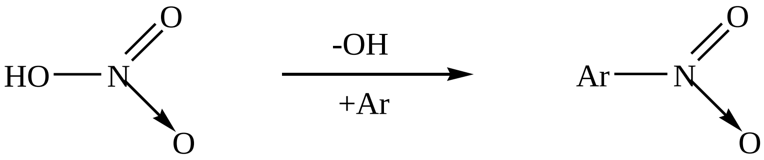
Course Code- CC10

Topic- Organic Chemistry, Nitrogen Compounds

ORGANIC COMPOUNDS OF NITROGENS:

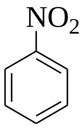
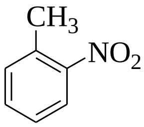
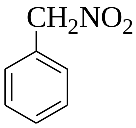
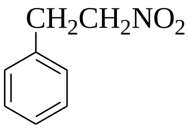
: Aromatic Nitro Compounds :

Aromatic nitro compounds may be considered to be the derivatives of aromatic hydrocarbons obtained by the replacement of nuclear hydrogen by nitro group. They may also be considered to be the derivatives of nitric acid in which the –OH group is replaced by an aryl group.



Nitric acid — Aromatic nitro compound

The aromatic nitro compounds may be either be nuclear substituted or side chain substituted. E.g.

Nuclear substituted		Side chain substituted	
			
Nitrobenzene	o-Nitrotoluene	Phenylnitromethane	1-(2-nitroethyl)benzene

- ## General methods of preparation of Aromatic nitro compounds:

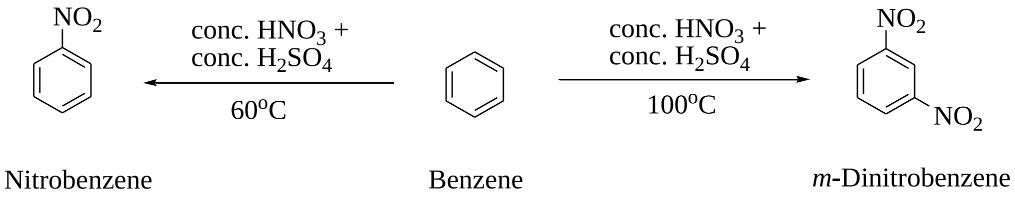
1. Direct Nitration:

Aromatic nitro compounds are prepared by direct nitration. Various reagents used for the purpose are:

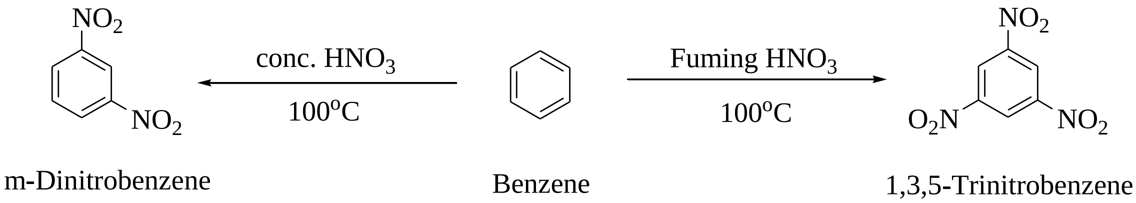
i. Concentrated nitric acid
ii. Fuming nitric acid containing 10% nitrogen peroxide
iii. Mixture of conc. nitric acid and conc. sulphuric acid
iv. Pyridinium nitrate in presence of pyridine
v. Liquid or gaseous nitrogen peroxide in presence of anhydrous aluminium chloride
vi. Acetyl nitrate

Not more than three nitro groups can usually be introduced into the nucleus. The number of nitro groups entering the nucleus depends upon:

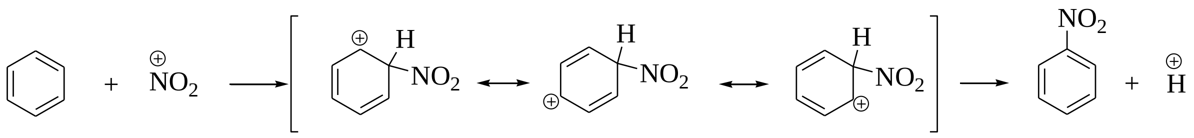
a) ***Temperature:*** Lower temperature favors the formation of mono-nitro, while the higher temperature favors the di-nitro derivatives.



b) ***Nature of nitrating agent***: At 100°C concentrated nitric acid introduces two nitro groups while fuming nitric acid introduces three nitro groups into the nucleus.

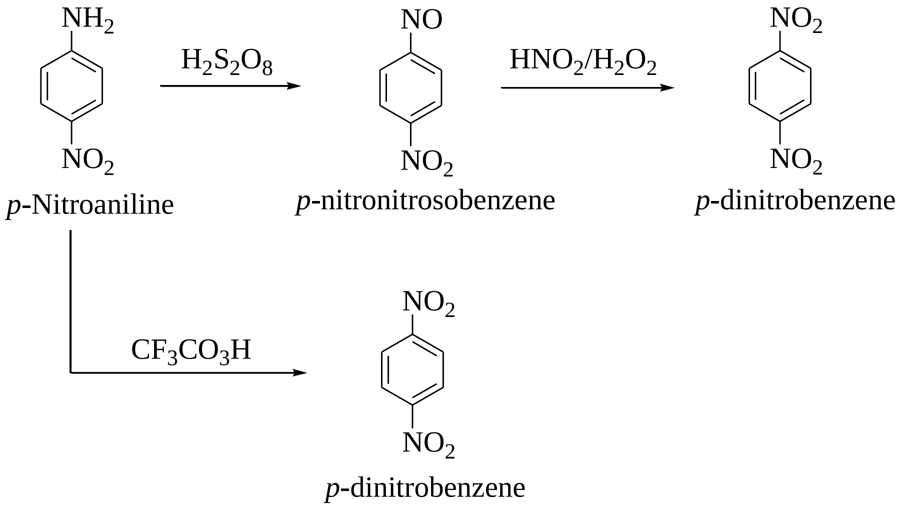


c) ***Nature of substance to be nitrated:*** Nitration is an electrophilic substitution reaction initiated by electrophilic species, nitronium ion, NO_2^+. The activating groups (e.g. $-CH_3$, $-NH_2$, -OH, etc.) which activates the ring accelerate nitration, while deactivating groups retard nitration.

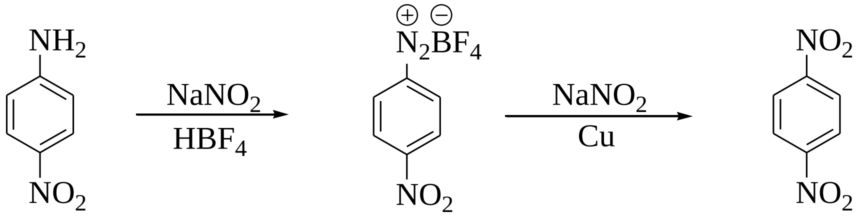


Mechanism of Nitration

2. Direct oxidation of an amino group to nitro group:



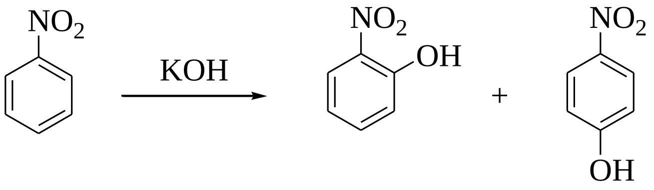
3. **Replacement of an amino group by nitro group via diazonium salt:**



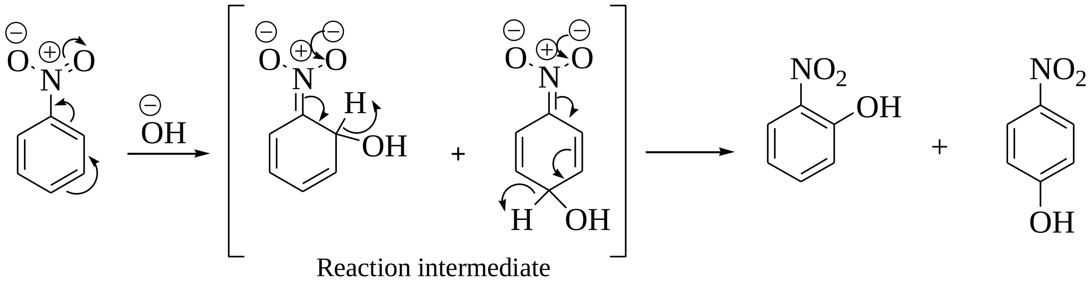
p-Nitroaniline Benzene diazonium fluroborate *p*-dinitrobenzene

• Chemical reactions of Nitro compounds:

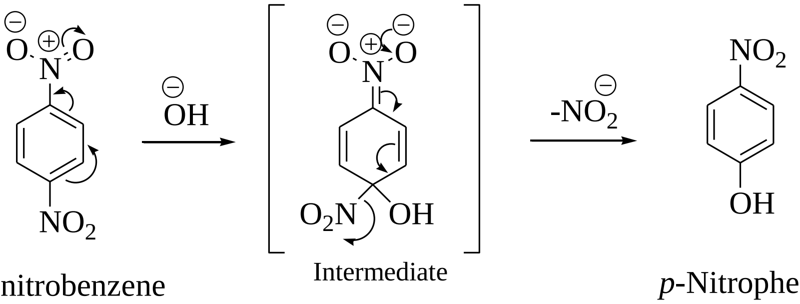
1. **Displacement of nitro group:**



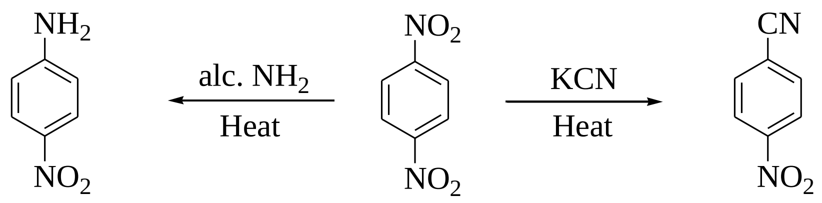
o-Nitrophenol *p*-Nitrophenol



Similarly,



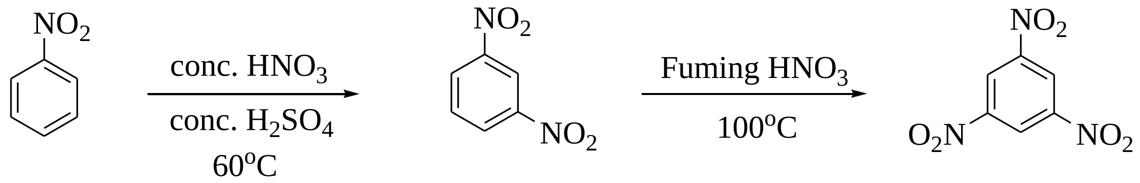
p-Dinitrobenzene *p*-Nitrophenol



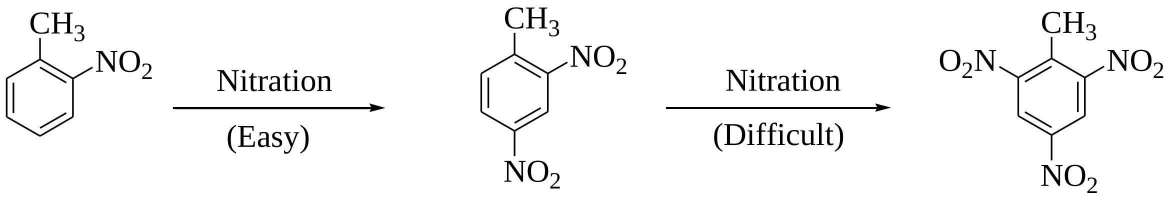
p-Nitroaniline *p*-Dinitrobenzene *p*-Nitrobenzonitrile

2. Electrophilic substitution:

In case of nitro compounds electrophilic substitution such as nitration, sulphonation, halogenation, etc. becomes difficult as the presence of nitro group deactivates the ring. However, presence of some activating group (-CH_3, -OH, -OR etc.) facilitates electrophilic substitution.



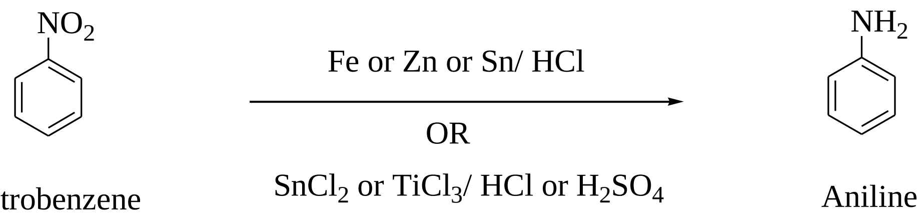
Nitrobenzene *m*-Dinitrobenzene 1,3,5-Trinitrobenzene



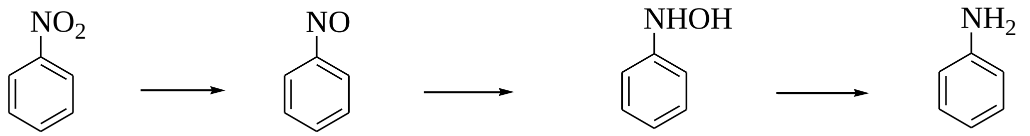
o-Nitrotoluene *m*-Dinitrobenzene 2,4,6-Trinitrotoluene

3. Reduction of nitro group:

(i) Reduction in acidic medium:

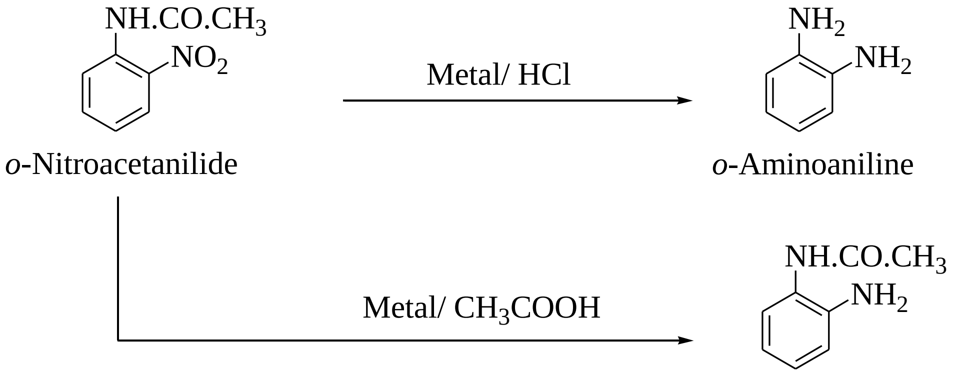


Nitrobenzene Aniline



Nitrobenzene → Nitrosobenzene → Phenylhydroxylamine → Aniline

During reduction, if there is any possibility of a group to get hydrolyzed, acetic acid is used in place of hydrochloric acid.



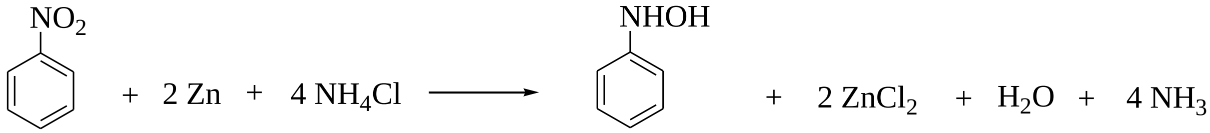
o-Nitroacetanilide

o-Aminoaniline

o-Aminoacetanilide

(ii) *Reduction in presence of Zn/ NH_4Cl:*

Zinc and ammonium chloride or zinc and calcium chloride reduce a nitro compound to hydroxylamine. Hydroxylamines are reducing agents and can reduce Tollen's reagent.

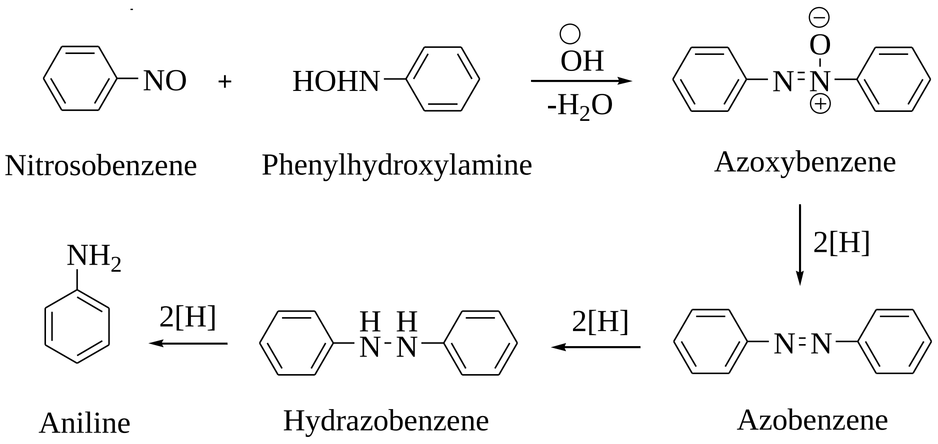


Nitrobenzene

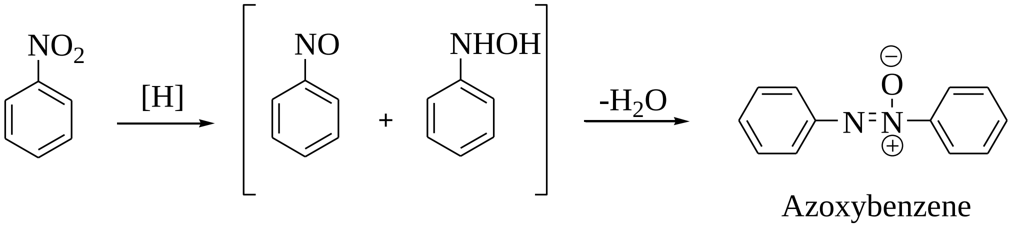
N-Phenylhydroxylamine

(iii) *Reduction in alkaline medium:*

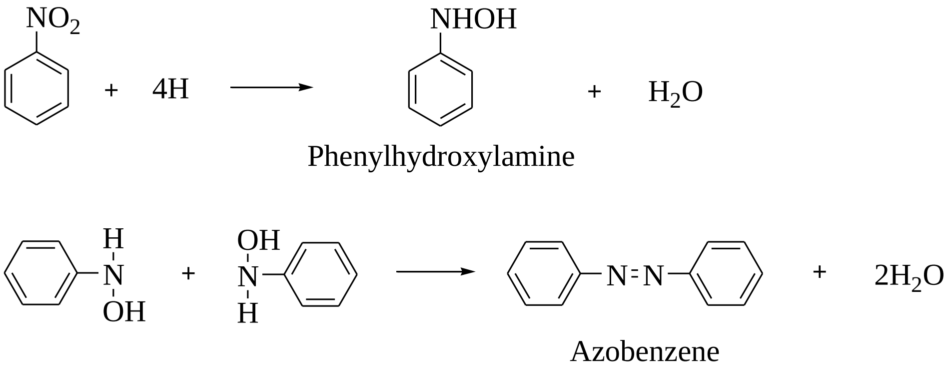
While acidic and neutral reduction result in the formation of mono-nuclear compounds, reduction in alkaline medium yields a variety of binuclear compounds due to the interaction of nitroso- and hydroxylamine derivatives formed during the reduction. The end compounds of reduction depend on the nature of reducing agents.



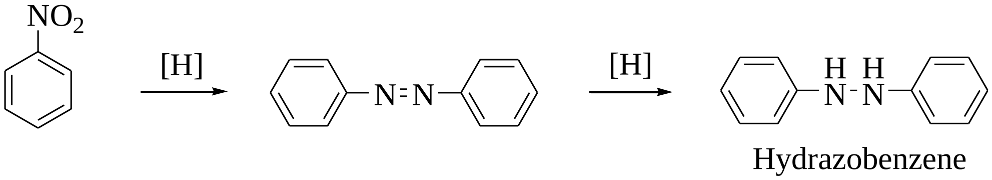
Reduction of nitrobenzene by methanolic sodium methoxide, glucose and sodium hydroxide or alkaline sodium arsenite forms azoxybenzene (85% yield).



Nitrobenzene when reduced with alkaline sodium stannite or zinc and methanolic sodium methoxide, forms azobenzene (85% yield).

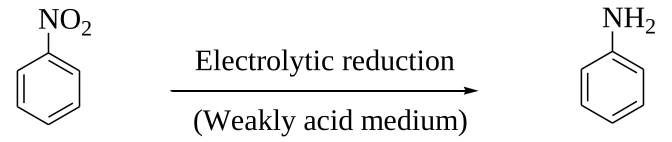


Nitrobenzene when reduced with zinc dust and caustic potash solution, nitrobenzene leads to the formation of hydrazobenzene.

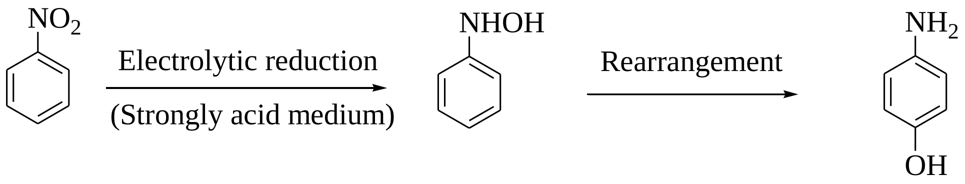


(iv) Electrolytic reduction:

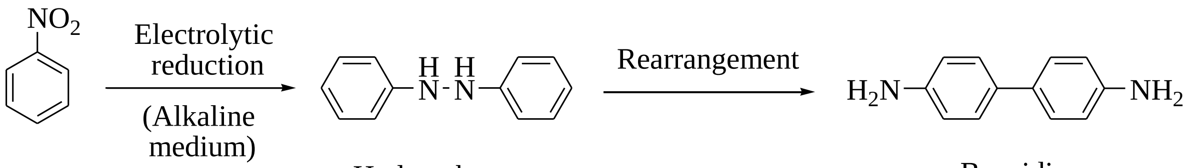
Electrolytic reduction reaction of nitrobenzene proceeds through the same stages as discuss above, but the nature of the final product depends upon the pH of the reaction medium.



Nitrobenzene Aniline



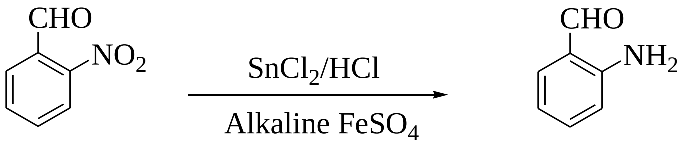
Phenylhydroxylamine *p*-Aminophenol



Hydrazobenzene Benzidine

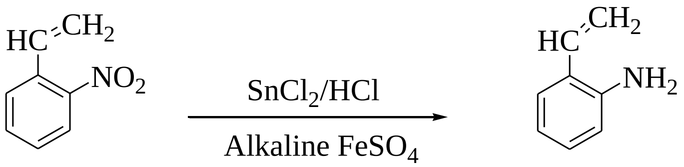
(v) Selective reduction of substituted nitro or polynitro compounds:

(a)



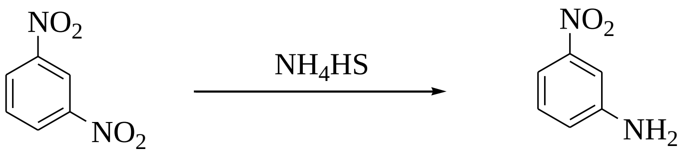
o-Nitrobenzaldehyde *o*-Aminobenzaldehyde

(b)



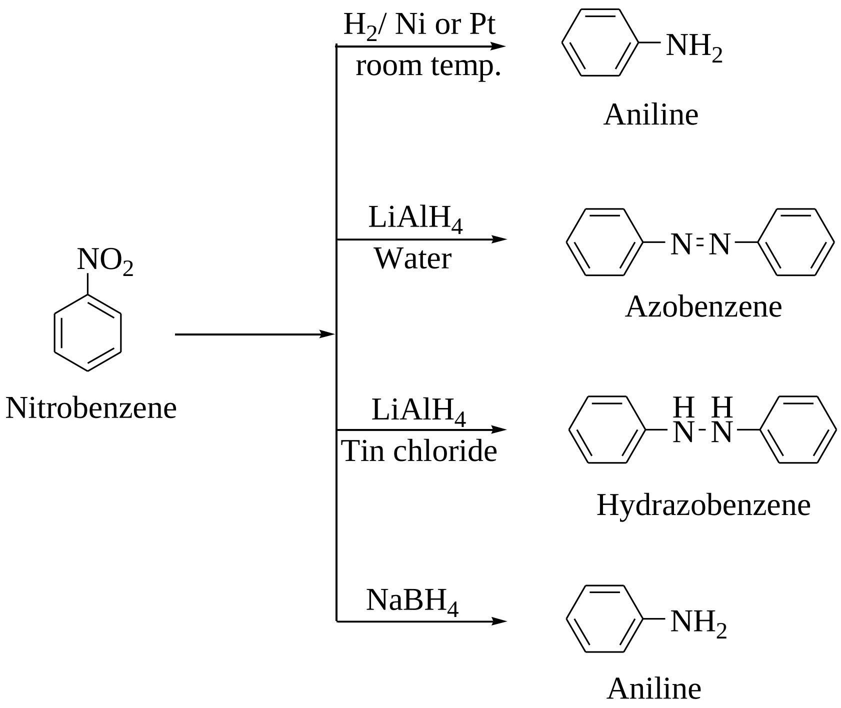
o-Nitrostyrene *o*-Aminostyrene

(c)



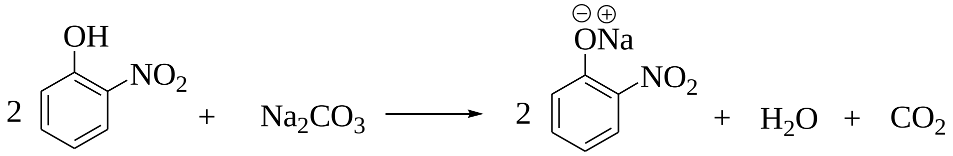
m-Dinitrobenzene *m*-Nitroaniline

(vi) Catalytic reduction:

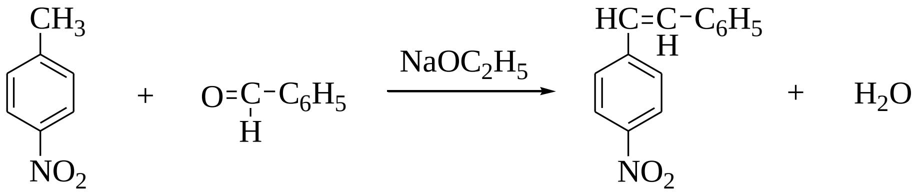


4. Effect of nitro group on other nuclear substituents:

(a) The acidic character of phenolic group is markedly enhanced by the presence of nitro group in *ortho*- or *para*- position. Thus phenol is feebly acidic and dissolves in sodium hydroxide, but does not give effervescence with sodium carbonate, whereas nitro phenols are acidic enough to give effervescence with sodium carbonate solution. Similarly, 2,4,6-trinitrophenol (picric acid) is still more acidic.

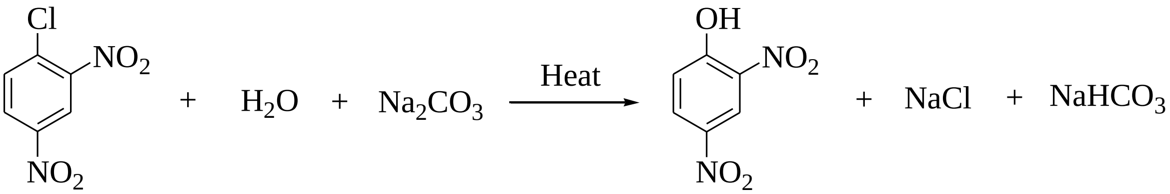


(b) The alkyl groups get activated by the presence of one or more nitro groups at ortho- or para- position, e.g.,



p-Nitrotoluene *p*-Nitrostilbene

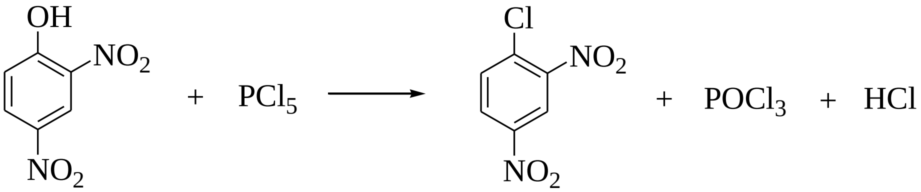
(c) A nuclear halogen atom gets activated and may be easily replaced, if one or more nitro groups are present at *ortho*- or *para*- position with respect to halogen atom.



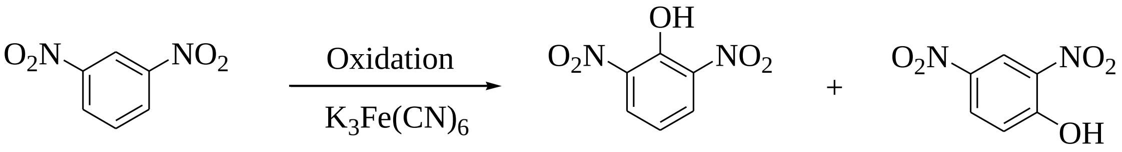
2,4-dinitrochloro-
benzene

2,4-dinitrophenol

(d) With phosphorus pentachloride phenol gives a poor yield of chlorobenzene, while nitro phenols containing nitro group in *ortho*- or *para*- position or both with respect to phenolic group form chloro derivatives in excellent yield.



(e) Hydroxyl group cannot be satisfactorily introduced into the nucleus by direct oxidation of benzene or nitrobenzene but the same is possible in casa of m-dinitrobenzene or 2,4,6-trinitrobenzene.



m-Dinitrobenzene 2,6-Dinitrophenol 2,4-Dinitrophenol