CHAPTER - 7 (Date: 2078/10/10.

'Nitro compound'

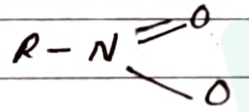
Introduction and Nomenclature.

Organic compounds containing nitro ($-NO_2$) as the functional group are called nitrocompounds. It is of two types:- Aliphatic nitrocompound and aromatic nitro compound

$R-NO_2$	$R-NO_2$
Aliphatic nitrocompound	Aromatic compound

- → 1°- nitroalkanes.
- → 2° - nitroalkanes.
- → 3°- nitro alkanes

→ Nitro group is isomeric with Nitrite.



$R-O-N=O$

Alkyl nitrite

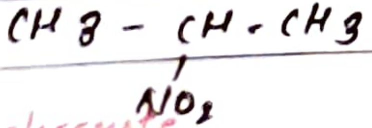
·Nitroalkane

Nomenclature :-

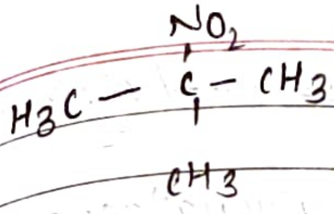
→ Nitro compounds are solely (singly) nombed by using IUPAC system. Nitro compounds are name by using prefix nitro.

→ Accordingly aliphatic nitrocompounds are called nitroalkanes while aromatic nitrocompounds are called nitroarenes

→ The position of the nitro groups and other substituent are indicated by number i.e 1,2,3... etc with the carbon atom bearing the nitro group getting the possible lowest number

Compounds	Nomenclature
CH_3-NO_2	Nitromethane
$CH_3-CH_2-NO_2$	Nitro-ethane
$CH_3-CH_2-CH_2-NO_2$	1 - Nitro propane
 $CH_3-\underset{\displaystyle NO_2}{\underset{\vert}{CH}}-CH_3$	2- Nitro propane

phatic

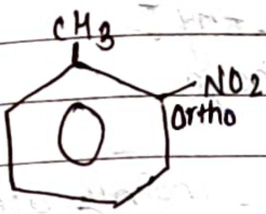


$H_3C-C(NO_2)(CH_3)-CH_3$

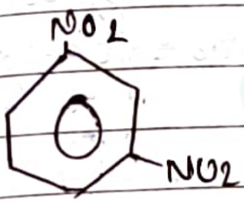
2- methyl 2- nitropropane.

Aromatic

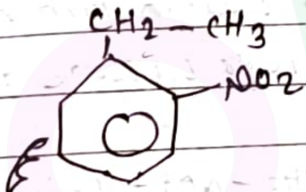
Nitrobenzene



2- Nitrotoluene or o-Nitrotoulene.

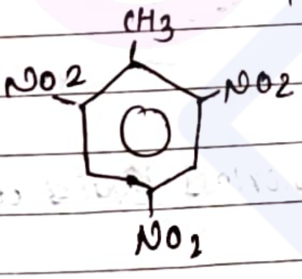


1,3-Dinitrobenze.

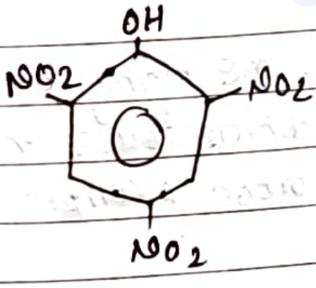


2- Nitro ethyl benzene

~~2-nitrobenzene~~



2,4,6 -Trinitro toluene (TNT)



2, 4, 6 - Trinitro phenol (picric acid)

Preparation of Aliphatic Nitro compounds (nitroalkanes)

1. From alkyl halides (haloalkane) → when alkylhalides are treated with silver nitrite in presence of alcohol gives nitroalkane.

$$R-I + AgNO_2 \xrightarrow{Alcohol} R-NO_2 + AgI$$

Eg:-

$$CH_3-I + AgNO_2 \longrightarrow \underset{\text{Nitromethane}}{CH_3-NO_2} + AgI$$

ie. [illegible] This method is mainly used to prepare 1°-nitroalkanes and not applicable for prepn of aromatic nitro compounds.

2. From alkene → when alkane is heated with the fuming HNO_3 in the vapour phase at 150-400°c under pressure gives nitro alkanes.

$$\text{Eg:-}\quad CH_3 \vdots H + \underset{\text{fuming}}{OH \vdots NO_2} \xrightarrow{400°c} CH_3-NO_2 + H_2O$$

Physical properties →

1. physical state → Nitroalkanes are colorless liquid with pleasant smell.

2. Boiling points → The nitrocompounds are highly polar and thus have strong dipole-dipole interactions which cause them to have high boiling points than hydrocarbon of comparable molecular mass.

3. Solubility → Nitroalkanes are ([illegible]) sparingly soluble in water but soluble in organic solvents like alcohol, ether etc.

Chemical propertise of Nitroalkanes.

Reduction:- Nitro compounds are reduced to primary amines through the following cases:-

G.R:⇒ $$\mathrm{R-NO_2} \xrightarrow[-H_2O]{+2H} \underset{\text{Nitro compound}}{\mathrm{R-N=O}} \xrightarrow{+2H} \underset{\text{A substituted hydroxylamine}}{\mathrm{RNHOH}} \xrightarrow[-H_2O]{+2H} \underset{1^\circ \text{ amine}}{\mathrm{R-NH_2}}$$

Note:- The final product depends upon
- PH of reaction medium
- Nature of reducing ag.

a) Reduction in acidic medium:- when aliphatic nitrocompound are treated with active metals liken Zn, Fe or Sn and con c. HCl give primary amines.

Eg:-

$$\mathrm{CH_3-CH_2-NO_2 + 6[H]} \xrightarrow{Fe/HCl} \underset{\text{Ethanamine}}{\mathrm{CH_3CH_2-NH_2}} + 2H_2O$$

b) Reduction in Neutral medium → when aliphatic nitro compounds are heated with Zn/NH$_4$Cl/(aq) gives corresponding hydroxyl amines.

E.g:-

$$\mathrm{CH_3-NO_2 + 4[H]} \xrightarrow{Zn/NH_4Cl} \underset{\text{N-methyl hydroxylamine}}{\mathrm{CH_3-NHOH}} + H_2O$$

c) catalytic reduction :→ when aliphatic nitro compounds are treated with H_2(Ni) or H_2/Pt or H_2/Pd gives corresponding primary amines.

Eg:-

$$\mathrm{CH_3-CH_2-NO_2 + 3H_2} \xrightarrow{Ni\ or\ Pt} \mathrm{R-NH_2 + 2H_2O}.$$

ⓓ Reduction with lithium aluminium hydride →

e.g:-

$$CH_3-NO_2 + 6[H] \xrightarrow[ether]{LiAlH_4} CH_3-NH_2 + 2H_2O$$

Methanamine

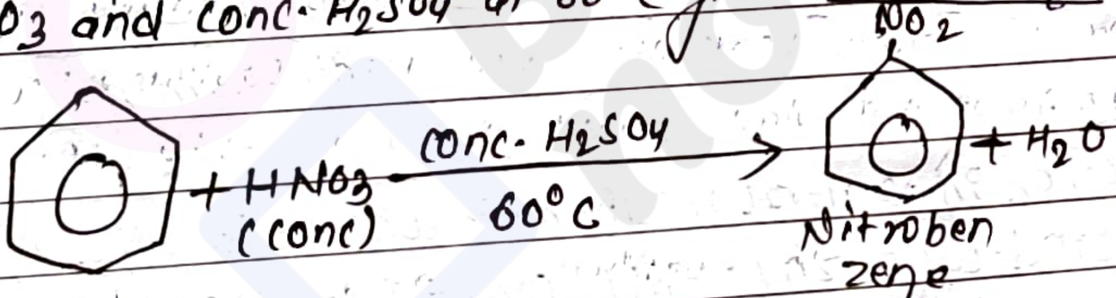
Uses:-

Nitroalkane
- used → To prepare amines.
- used → As solvents.
- used → To prepare dyes, drugs etc.

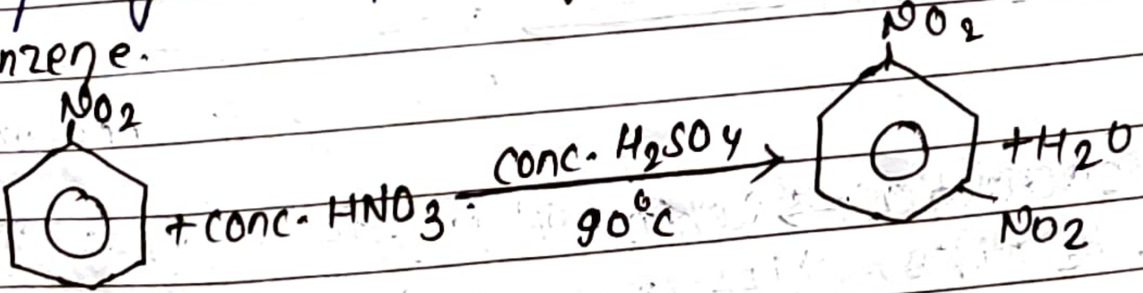
[B] Aromatic - Nitro Compounds. (Nitrobenzene)

Laboratory preparation of Nitrobenzene. ($C_6H_5NO_2$)

When benzene is heated in the presence of conc. HNO_3 and conc. H_2SO_4 at 60°C gives nitrobenzene



At Higher temperature further nitrated to give m-Dinitro benzene.



m- Dinitrobenzene

- **Procedure:** At first 60 ml of conc. HNO_3 & 60 mL of conc. H_2SO_4 are taken in a round bottomed flask then 50 ml of benzene is added gradually to the flask, a little at a time with shaking and cooling after each addition.

After addition of all benzene the mixture is refluxed on water bath at 60°c for about 1 1/2 hours till the yellow oily layer appears on the surface with bitter almond odour.

Purification:-

The upper layer is separated by separation funnel followed by washing with dil Na_2CO_3 to remove acidic impurities and then with water several times. After that it is dried over anhy. $CaCl_2$ & finally distilled at about 208°C - 212°C to obtain pure nitrobenzene.

* physical properties of nitrobenzene :

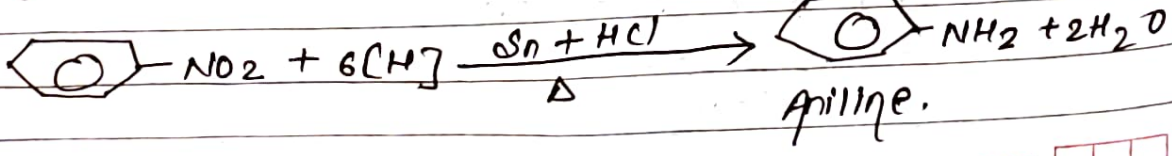
1. It is pale yellow oily liquid with smell of bitter almonds.
2. It is insoluble in water but soluble in organic solvents.
3. It has bpt : 210 °c and specific gravity 1.2.
4. It is highly toxic since its, vapours is readily absorbed by skin.

* CHEMICAL PROPERTIES OF NITROBENZENE (IMPORTANT)

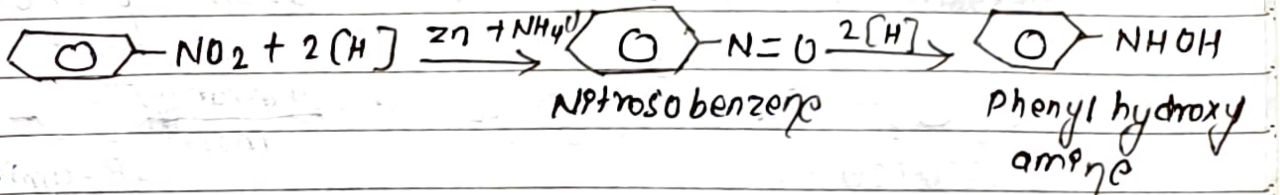
A. Due to nitro group:-

1. Reduction:

a) Reduction in acidic medium → when nitrobenzene reacts with active metals like Zn, Fe or Sn in the presence of conc. HCl gives aniline.



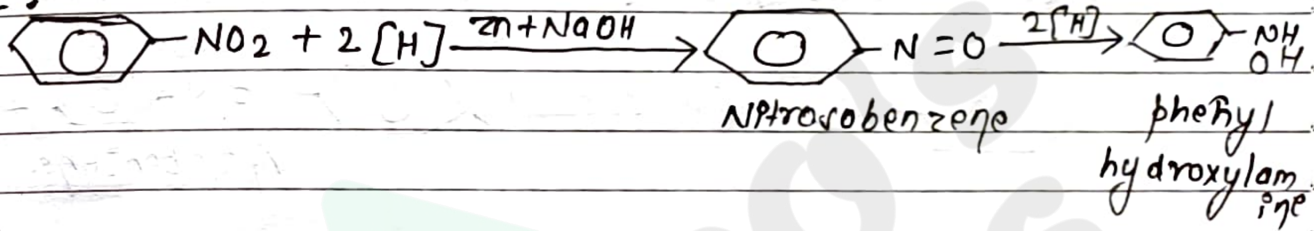
b) Reduction in neutral medium → when nitrobenzene reacts with zn / NH_4cl (aq) gives phenyl hydroxyl amine.



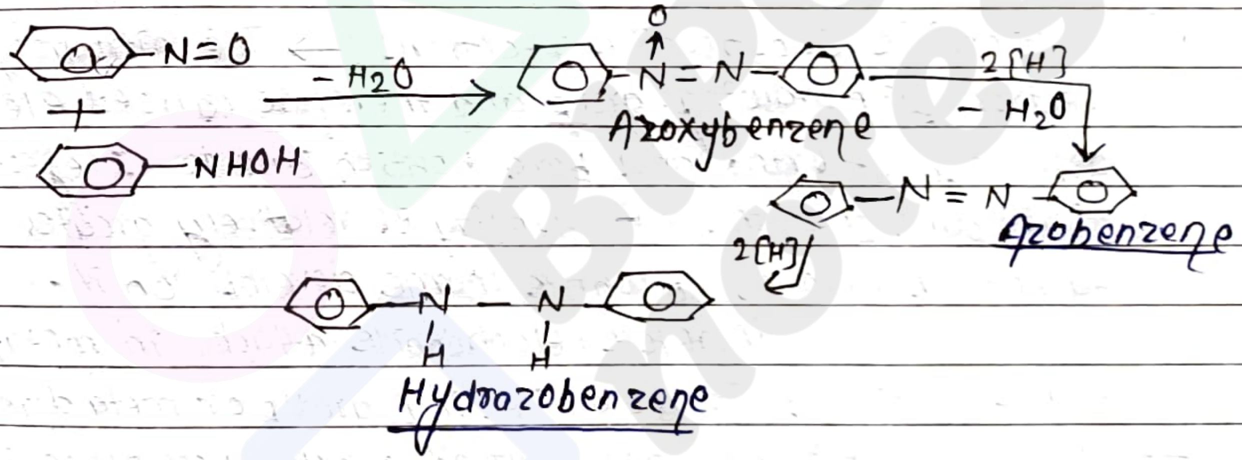
v. imp.

ⓒ Reduction in alkaline medium → when nitrobenzene reacts with zn and NaOH gives hydrozobenzene via azoxybenzene and azobenzene.

step - I ⇒

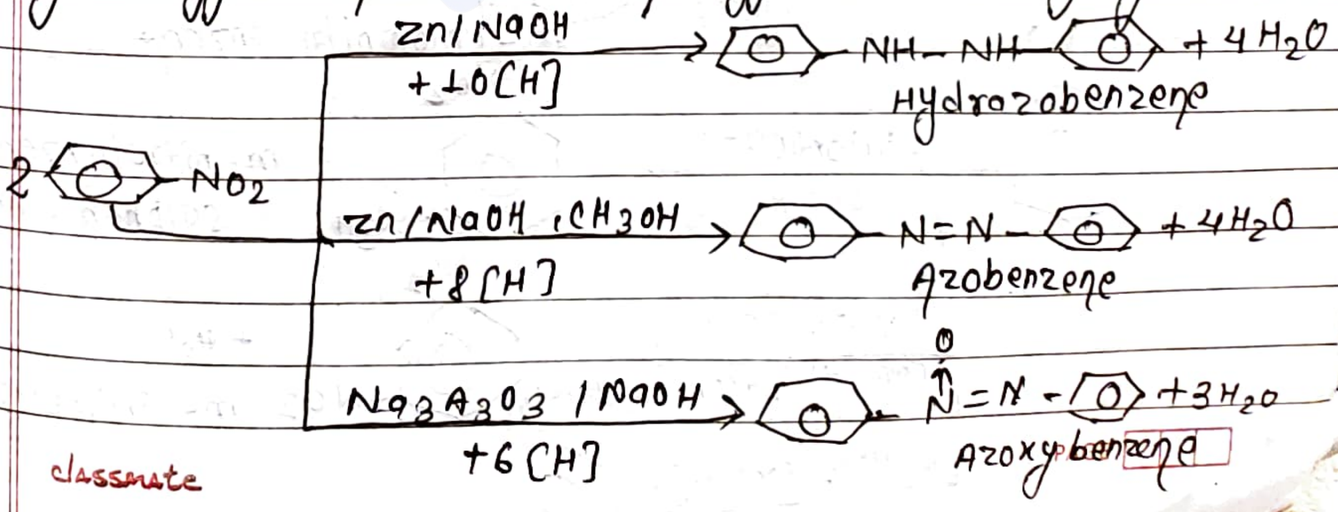


step - II ⇒

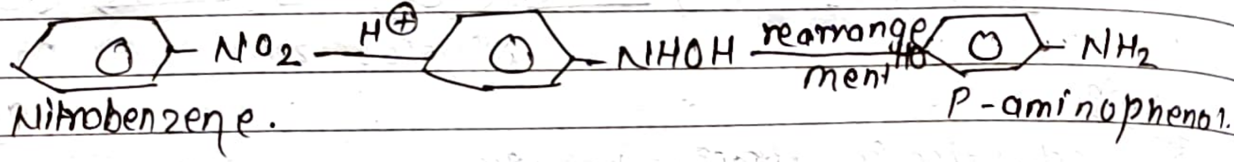


Note:

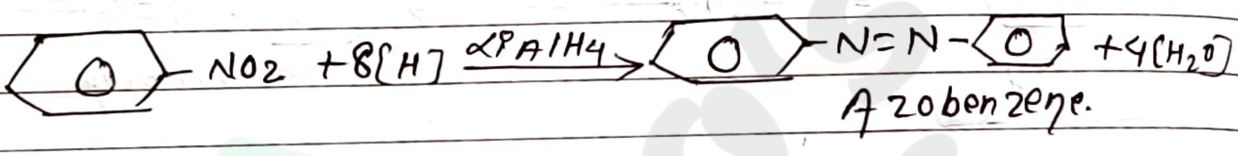
→ Thus, bimolecular reductions takes in alkaline medium to give different products, with different reducing agent.



(d) Electrolytic reduction → when nitrobenzene is reduced electrolytically in the presence of acid, yields phenylhydroxylamine, which rearranges to p-aminophenol.

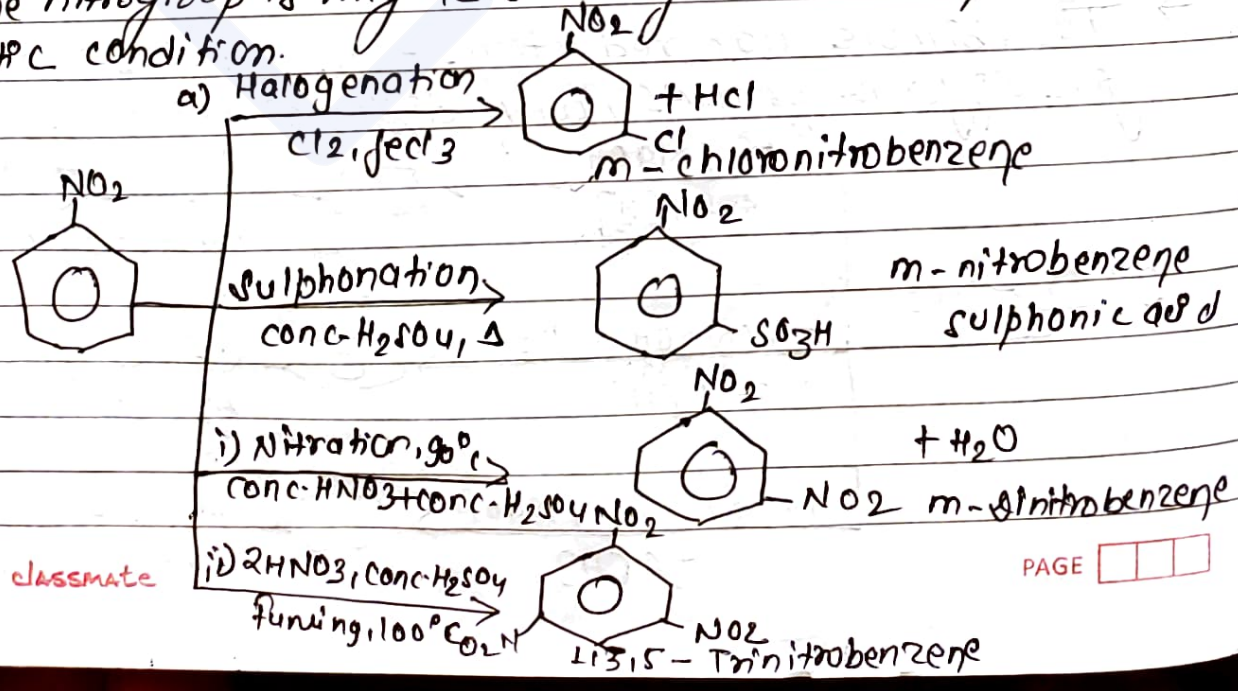


(e) Reduction with lithium aluminium hydride → when nitrobenzene reduced with LiAlH4, yields azobenzene.



[B] Electrophilic substitution reactions :→ The nitrogroup is electron withdrawing group and therefore causes electron deficiency at ortho and para position due to -I effect and it is found that the e⊖ density is relatively greater in meta position because no positive charge develops on it.
Therefore, electrophile attacks in metaposition.
Hence nitrogroup in meta directing group or meta director.

→ the nitrogroup is ring deactivating so rxn takes place in drastic condition.



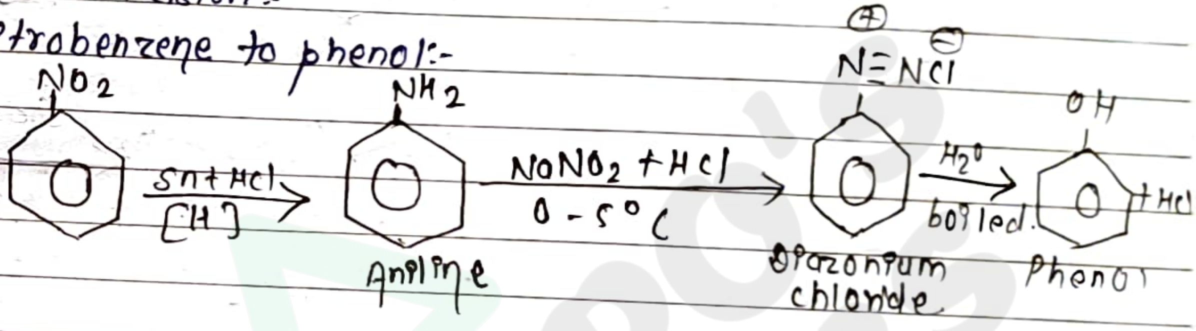
Uses:-

1) For manufacture of aniline.
2) For various aromatic compounds used in detergents, dyes and other pharmaceutical.
3) Manufacture of explosive eg:- TNT, TNBC 1,3,5-Trinitrobenzene Rox (Research and Development explosives)
4) Used as high boiling inert solvent.
5) Used as scent for cheap soaps.

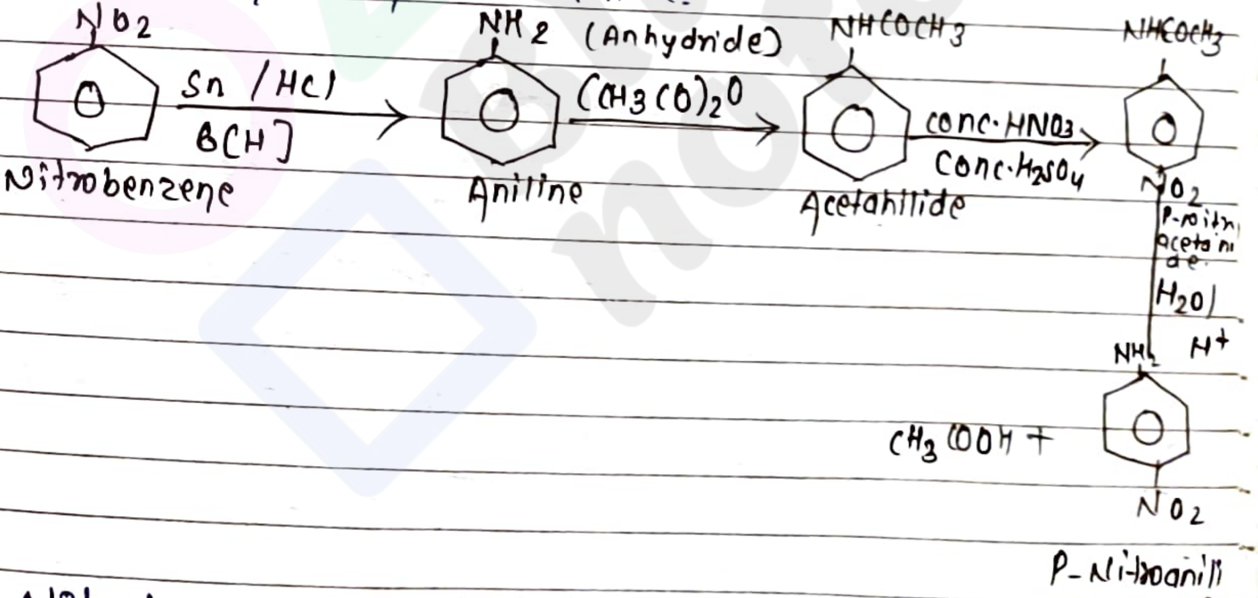
Question

Conversion:-

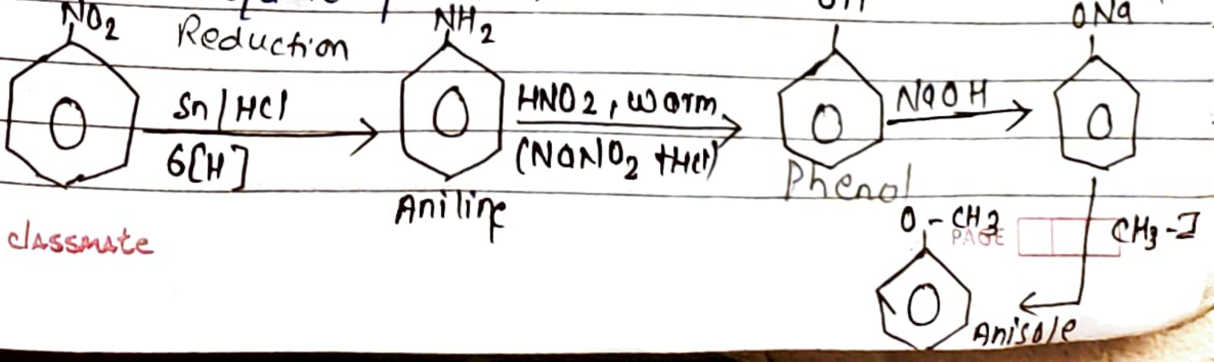
1. Nitrobenzene to phenol:-



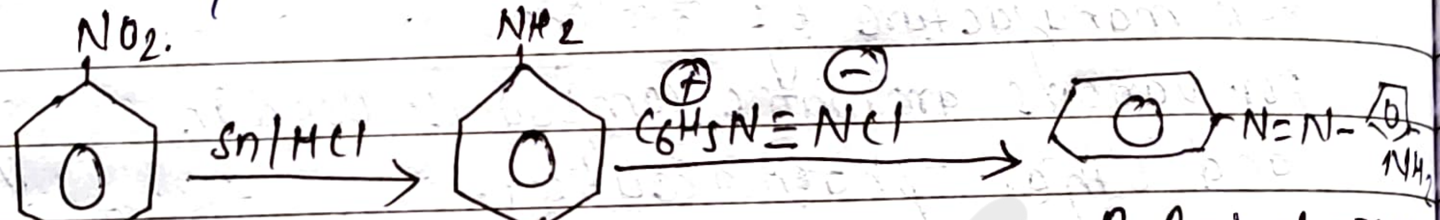
2. Nitrobenzene to p-Nitroaniline:-



3. Nitrobenzene to Anisole:→

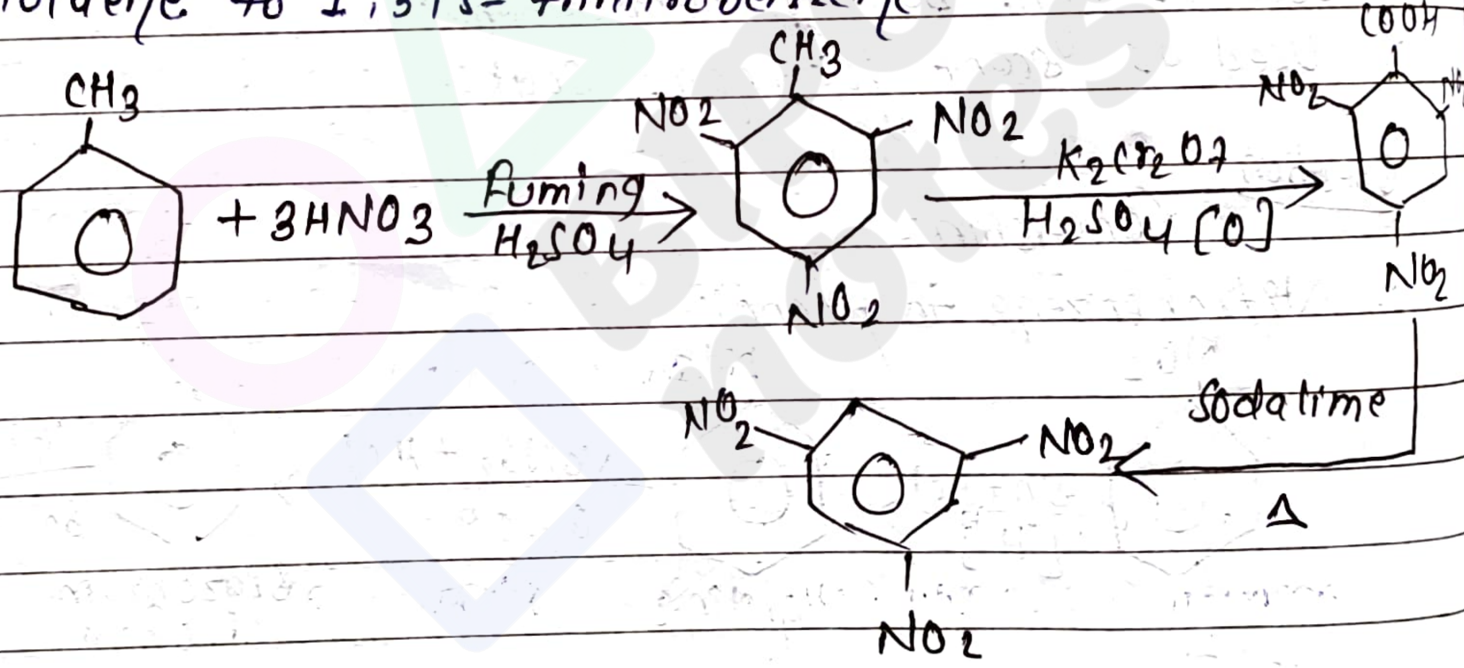


4. Nitrobenzene to P- aminobenzene.



P-Aminobenzene

5. Toluene to 1,3,5- trinitrobenzene.

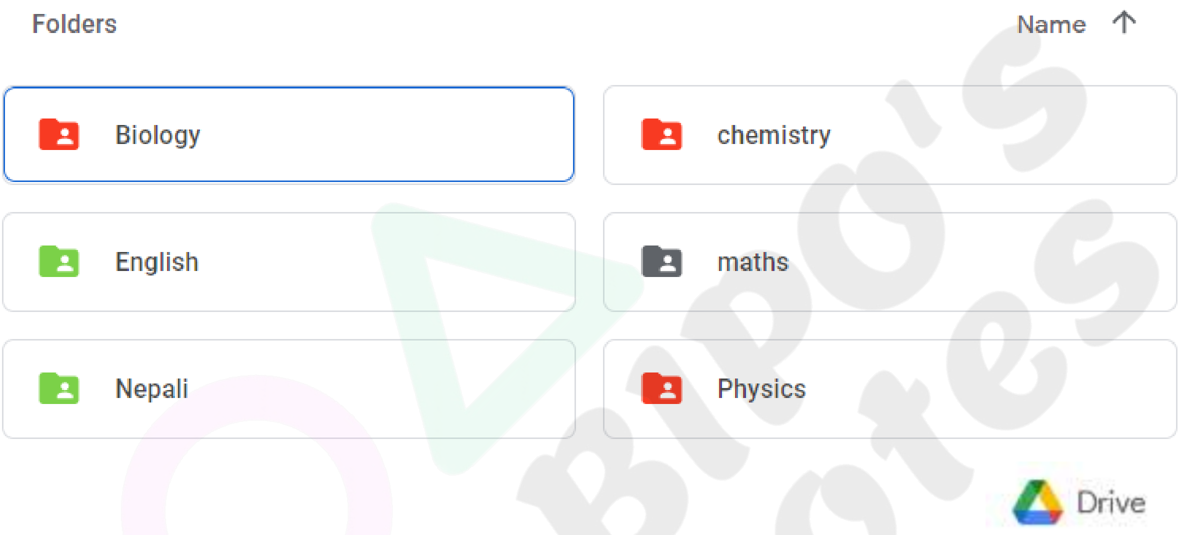


1,3,5- Trinitrobenzene.

Bipin Khatri

(Bipo)

Class 12 complete notes and paper collection.



Feedbacks:

admin@bipinkhatri.com.np | bipinkhatri.ram@gmail.com

Contact:

@im.bipo www.bipinkhatri.com.np @im.bipo