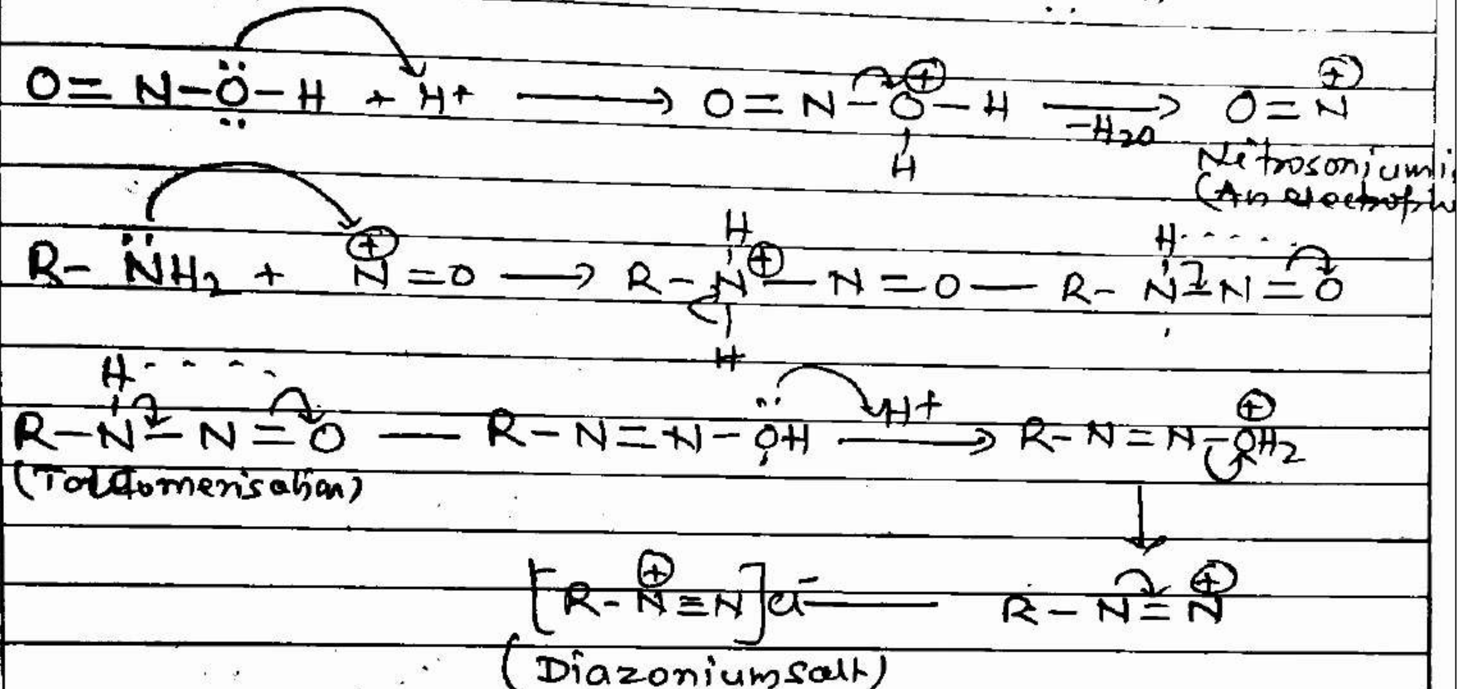
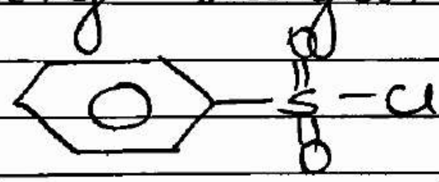
Mechanism of the reaction:→

Str. of Nitrous acid: $:\ddot{O}=N-\ddot{O}-H$



(b) Reaction with Arylsulphonyl chloride or Hinsberg reagent:→



Benzenesulphonylchloride (Hinsberg reagent)

Aim: Hinsberg reagent or benzenesulphonyl chloride is used to identify or to distinguish Primary (1°) amine, Secondary (2°) amine & tertiary (3°) amine.

theory:→ Hinsberg reagent (Benzenesulphonyl Chloride) react with primary amine

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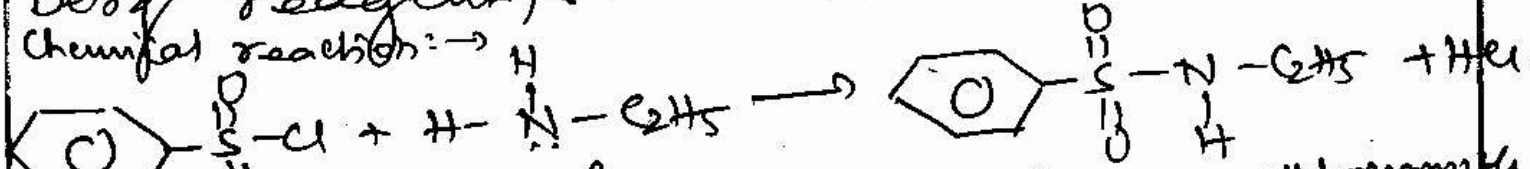
i.e ethylamine to give N-ethyl benzenesulphonamide (having one acidic hydrogen which is bonded with nitrogen) so it will dissolve in alkali like NaOH or KOH.

When 2° amine like N-ethyl ethanamine react with Hinsberg reagent (Benzenesulphonyl Chloride) it form N,N-diethyl benzenesulphonamide (having no acidic hydrogen bonded to nitrogen) which is insoluble in alkali like NaOH.

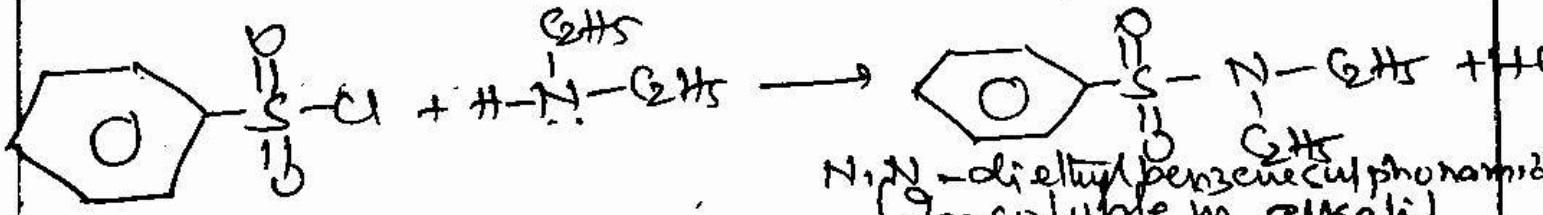
Tertiary amine do not react with Hinsberg reagent or Benzenesulphonylchloride.

In this way 1°, 2° & 3° amine can be separated by the help of Benzenesulphonyl chloride (Hinsberg reagent).

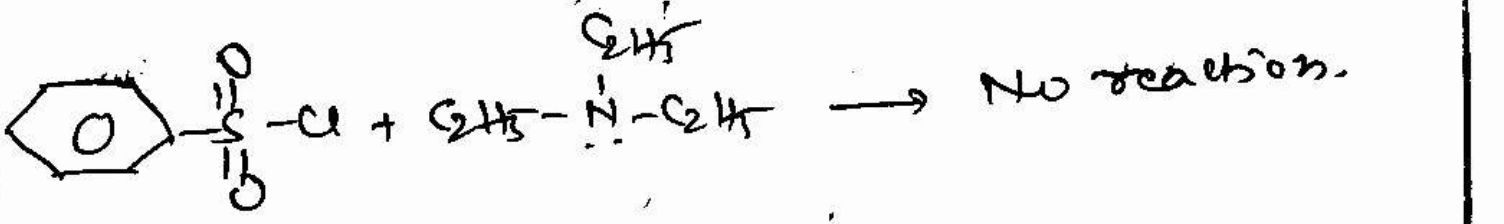
Chemical reaction:→



Benzenesulphonyl Chloride (Ethylamine) N-ethyl Benzenesulphonamide (Soluble in alkali due to presence of acidic hydrogen)



N,N-diethyl benzenesulphonamide (Insoluble in alkali)

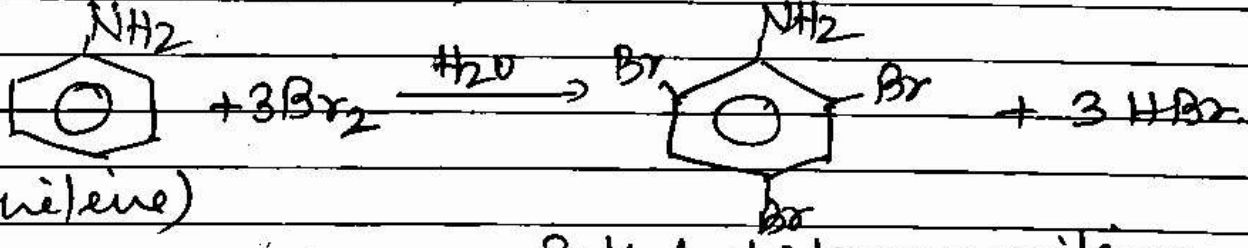


Electrophilic Substitution reaction: →

In these reactions at first electrophile is generated and this electrophile as a reagent attacks on substrate (i.e aniline) and one H atom is substituted followed according to resonance and shift itself there, that why reaction is called electrophilic substitution reaction. $\ddot{N}H_2$ group is activating group so it is o, p directing group, but in acidic midium (mainly in nitration) anilium ion is formed which is deactivating group so it form meta product also.

1. Bromination: →

When aniline is treated with Br_2 water at room temperature to give white precepitate of 2,4,6 tribromo aniline.



(Aniline)

2,4,6-tribromo aniline.

In above br condition product is trisubstituted, if we want monosubstituted product then we have to do protection of NH_2 group by using acetylation with acetic anhydride. Due to acetyla-

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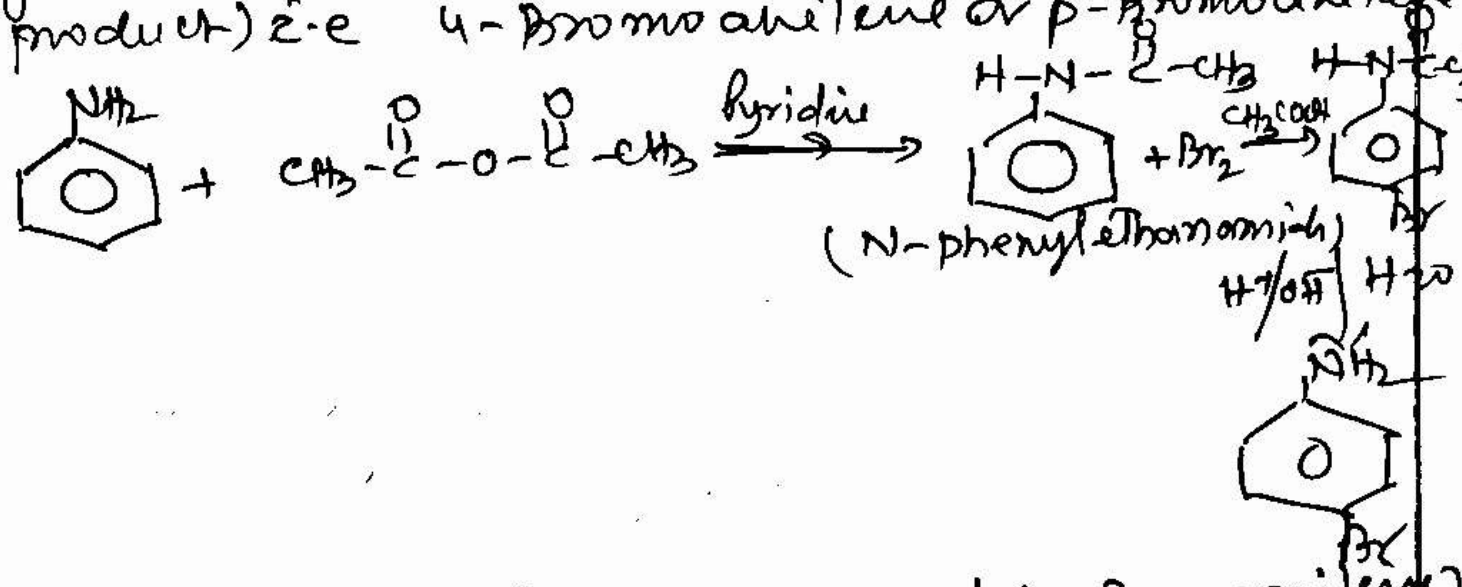
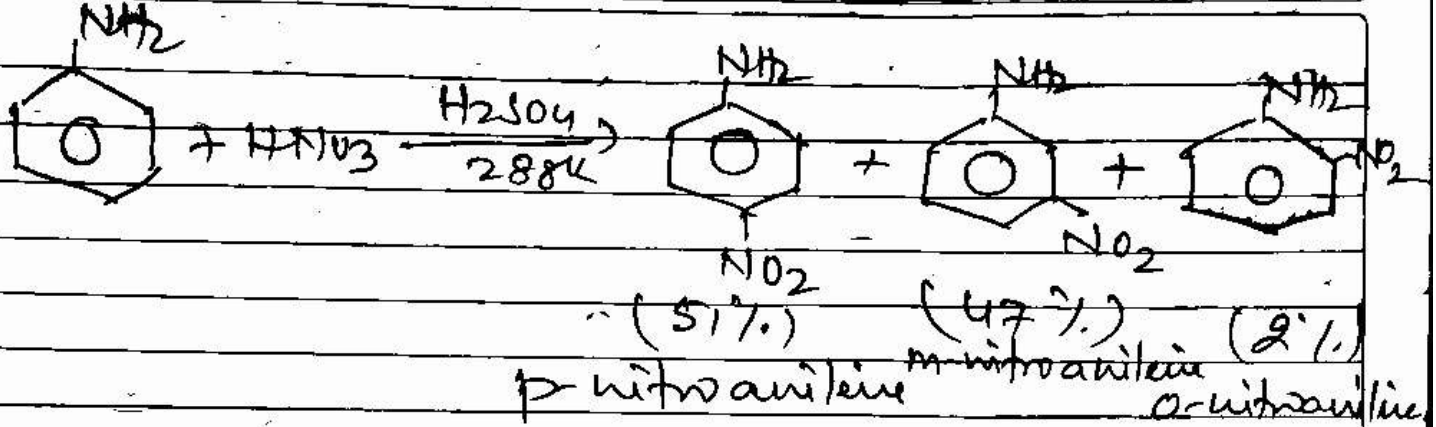
by the help of acetic anhydride to first amide is formed which on hydrolysis it gives substituted aniline (Monosubstituted product) i.e 4-Bromoaniline or p-Bromoaniline.



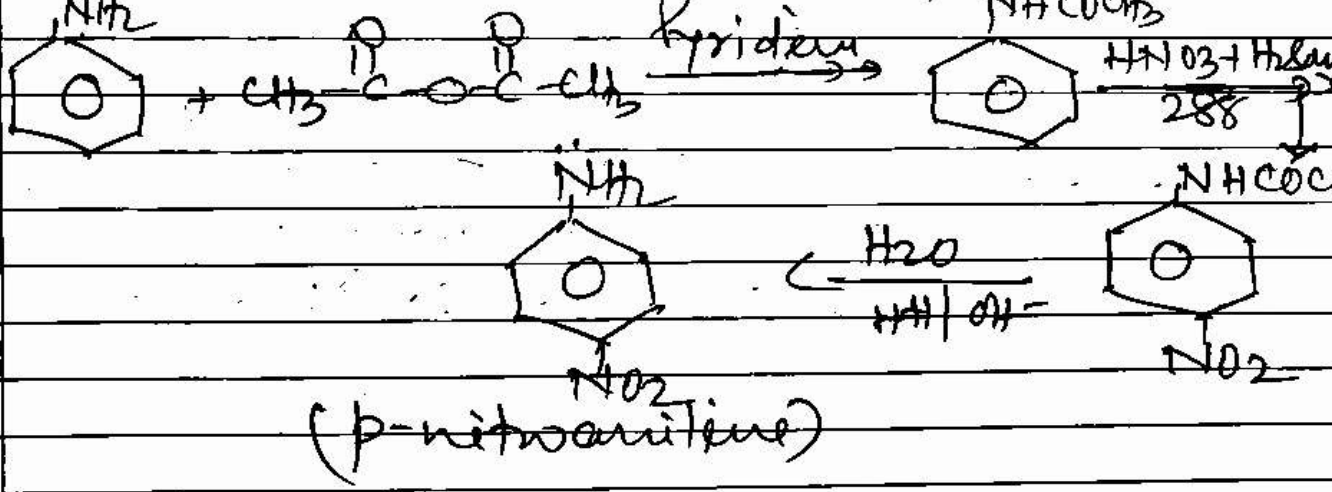
11. Nitration reaction :-

When aniline react with conc. Nitric acid in presence of Conc. H_2SO_4 and heat it form o, m, p nitroaniline. Actually NH_2 group is activating group & o, p directing group but in presence of acid (H+) NH_2 converts into $\overset{+}{N}H_3$ (anilinium ion) which is deactivating group & meta-directing group. Due to steric hindrance ortho product is very less i.e 2%, & para product is major product i.e 51% and the meta product is 47% approx.



(51%) p-nitroaniline (47%) m-nitroaniline (2%) o-nitroaniline

but when NH_2 group is protected by acetylation reaction with acetic anhydride then nitration reaction can be controlled and give desired product which is monosubstituted i.e p-nitroaniline.



(p-nitroaniline)

iii) Sulphonation reaction :→

Aniline react with Concentrated Sulphuric acid to form ~~acetic~~ anilinium hydrogen sulphate which on heating with sulphuric acid at 453 to 473K it gives - p- aminobenzene sulphonic acid or Sulphanilic acid.

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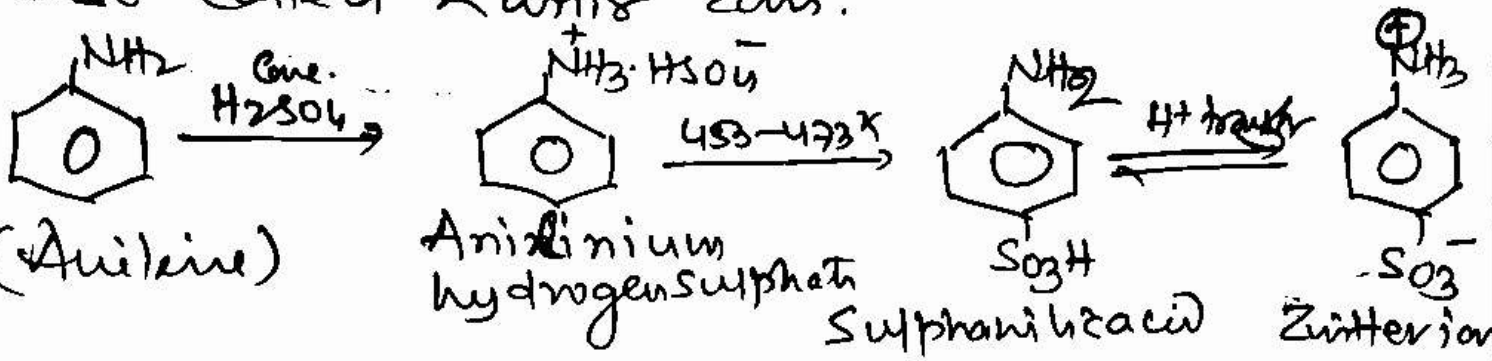
Sulphanilic acid shows proton transfer from SO_3H to NH_2 in this this way both group becomes charged and the molecule becomes bipolar which is also called Zwitter ion.



(Aniline) Anilinium hydrogensulphate Sulphanilic acid Zwitterion.

Note: Aniline do not show friedal Craft reaction (Alkylation or acetylation) because Anhy $AlCl_3$ is acidic in nature & aniline is base in nature so it react to form salt & prevent the reaction.

08/07/20