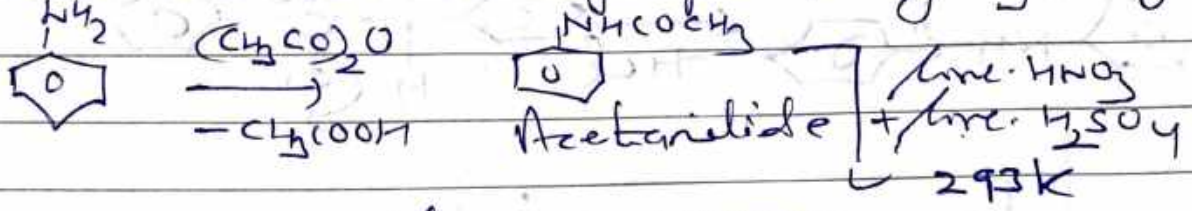
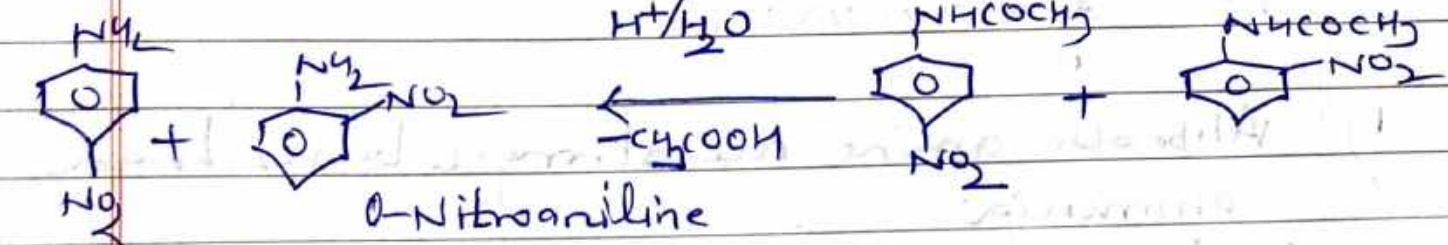
formn of m-bromo:

In strongly acidic conditions, aniline is converted into anilinium ion since $-\overset{+}{N}H_3$ is a m-directing group, therefore, an unexpected large amount of m-nitroaniline is obtained.

Sufficient + convenient method:

Protection of amino group by acetylation + then removal of acetyl group by hydrolysis.

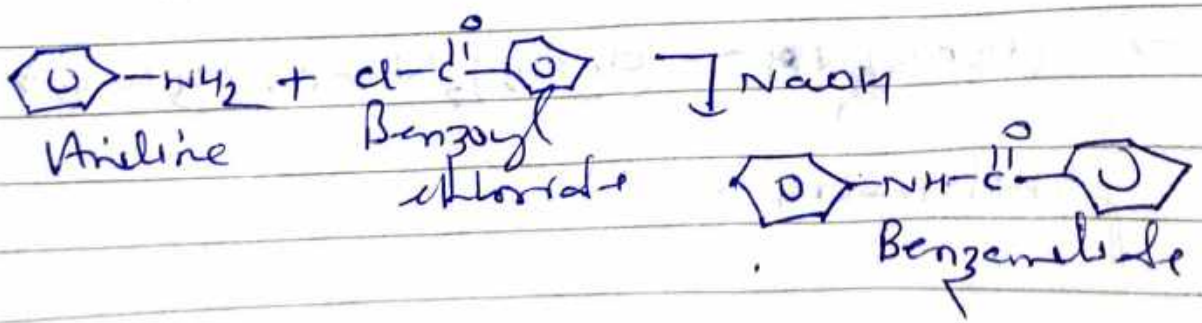




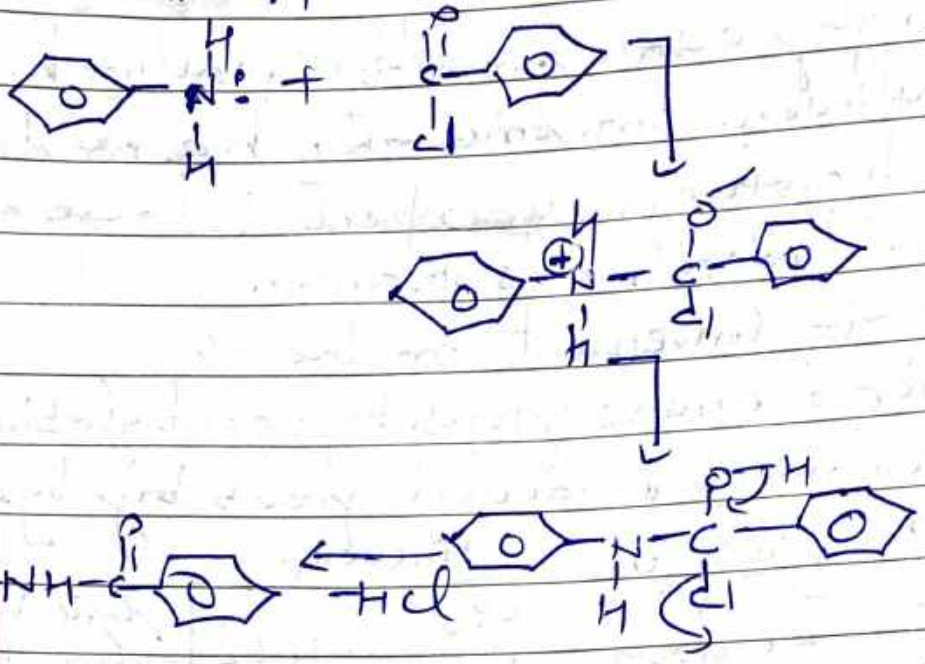
Schotten-Baumann Rxn:

The nucleophilic substitution of aromatic amines with acid chlorides results in the formation of N-substituted amides

Rxn of amines with benzoyl chloride is carried out in alkaline medium. This benzoylation rxn is called Schotten Baumann rxn



mechanism



Basicity of amines :

1) Aliphatic amines are stronger bases than ammonia

All three classes of aliphatic amines are stronger bases than ammonia as alkyl groups are electron donating groups.

Thus order should be

3° amines > 2° amines > 1° amine > NH_3

However, in aqueous soln's, a 2° amine is invariably more basic than 1° & 3° amines

→ $(CH_3)_2NH > CH_3NH_2 > (CH_3)_3N > NH_3$

→ $(CH_3CH_2)_2NH > (CH_3CH_2)_3N > CH_3CH_2NH_2 > NH_3$

Explanation

The basicity of an amine in aqueous soln depends upon the stability of the ammonium cation formed by accepting a proton from water.

- The stability of ammonium cation in turn depends upon:

1) +I effect of alkyl gps
2) Extent of H-bonding with water molecules
3) Steric effect of alkyl gp

+I effect	H-bonding
3° > 2° > 1°	More no. of H-atoms present on Nitrogen atom more will be H-bonding 1° > 2° > 3°

Steric factor
1° > 2° > 3°

→ In $-CH_3$, H-bonding predominates
→ In $-C_2H_5$ or bigger +I effect predominates

Note

In non-aqueous solvents (chlorobenzene) in gaseous phase, the stabilization of conjugate acid via H-bonding is absent hence stability depends upon Inductive effect

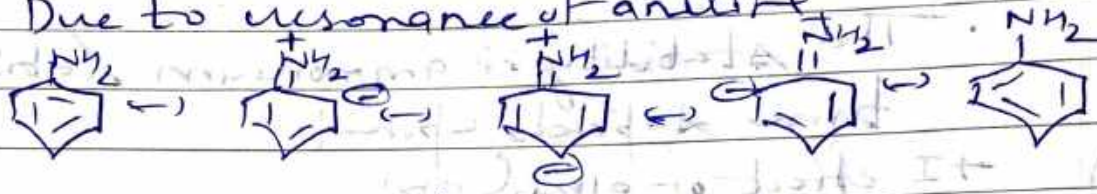
$3° > 2° > 1° > NH_3$

Basicity of Aromatic amines:

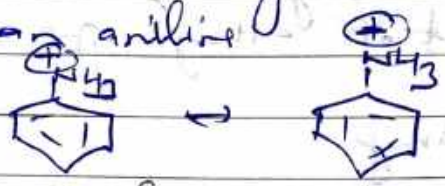
Aromatic amines are far less basic than ammonia & aliphatic amines.

Reasons:

1) Due to resonance of aniline



2) Lower stability of anilinium ion than aniline



In case of ammonia & aliphatic amines, delocalization of lone pair of electrons on the nitrogen atom by resonance is not possible.

Effect of substituents

→ Electron donating groups such $-CH_3$, $-OCH_3$, $-NH_2$ increases the basicity

→ $-NO_2$, $-CN$, $-SO_3H$, $-COOH$, $-X$ decreases the basicity

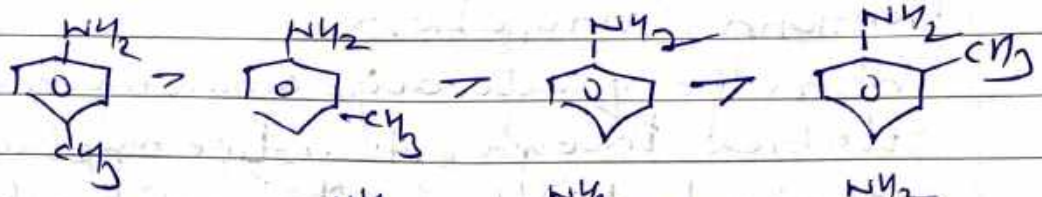
Note:

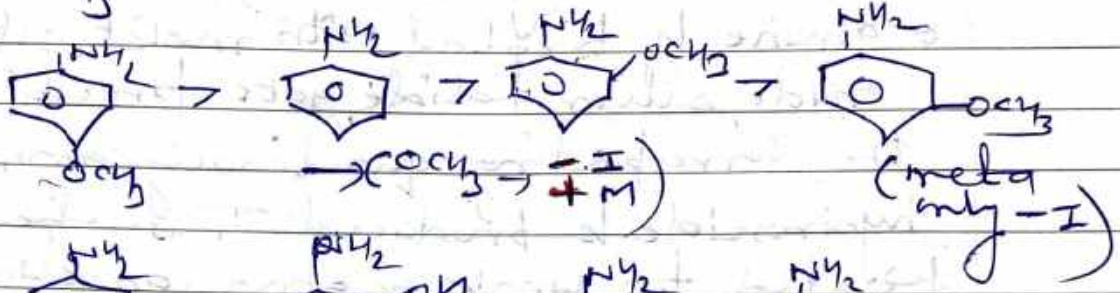
1) Electron donating gp stabilizes conjugate acid

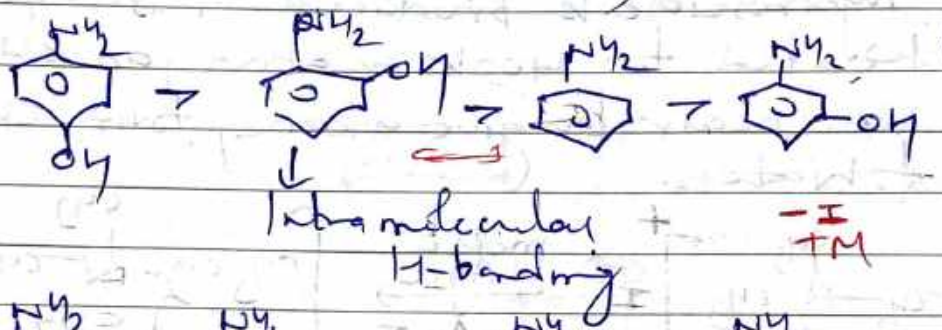
2) The base strengthening & base weakening effect is more marked at p-position than in

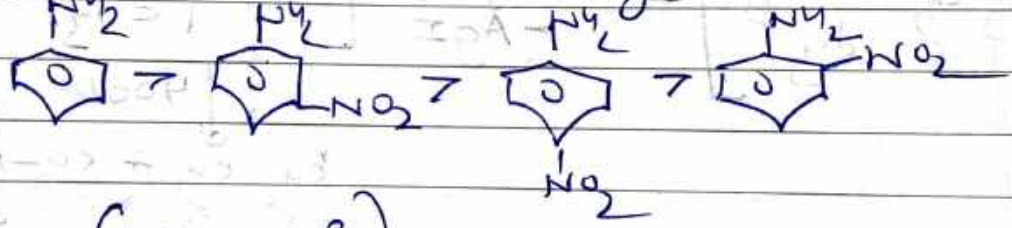
3) O-substituents are usually weaker than aniline regardless of nature

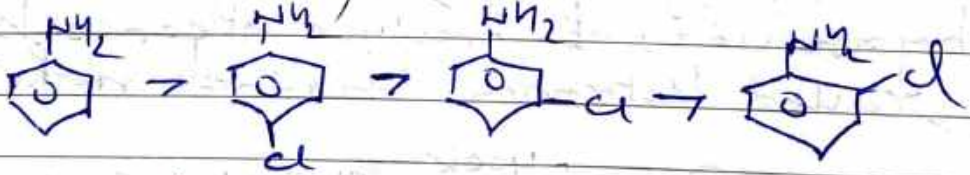
of Electron donating & Electron withdrawing group. Ortho effect is due to steric & electronic factor

1) 

2) 

3) 

4) 

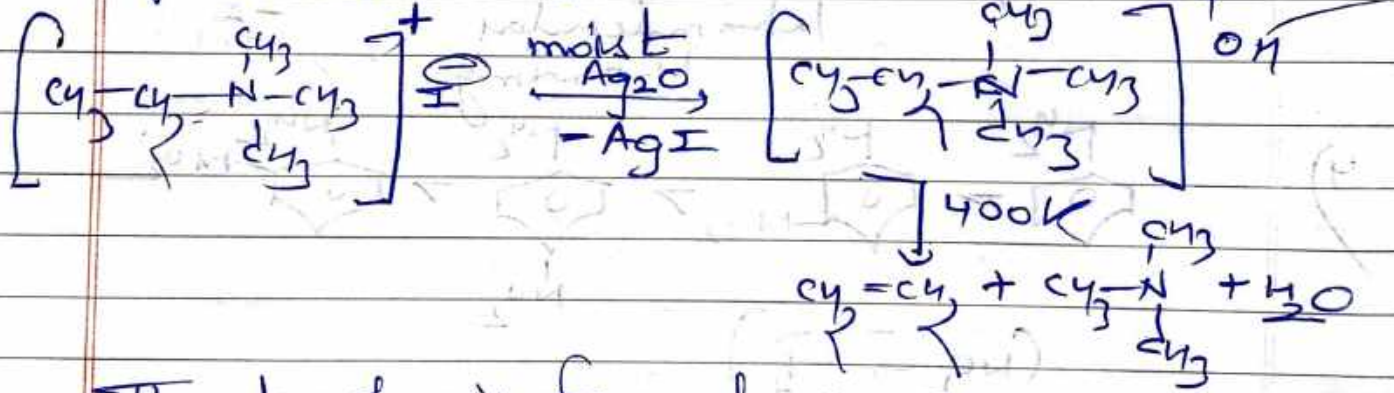
5) 

6) $C_6H_5CH_2NH_2 > C_6H_5NH_2$

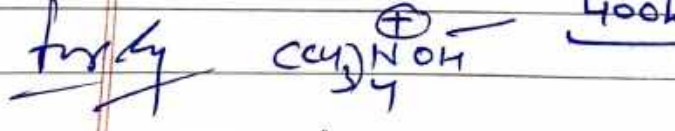
Hofmann Versus Saytzeff Elimination reaction :-

Hofmann Elimination

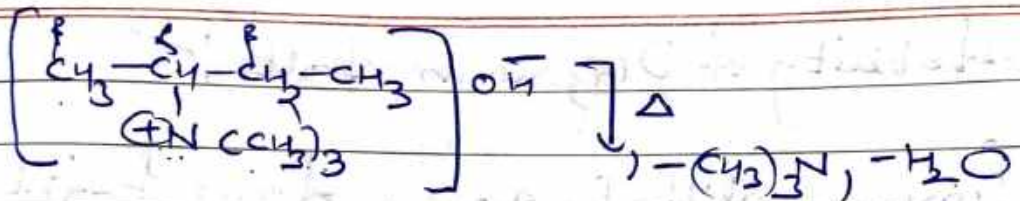
When the quaternary ammonium halide obtained through exhaustive methylation of amine is treated with moist silver oxide, silver halide gets precipitated & the corresponding quaternary ammonium hydroxide is produced. This when heated to 400K or above, an elimination rxn occur to give alkene, trimethylamine & Water.

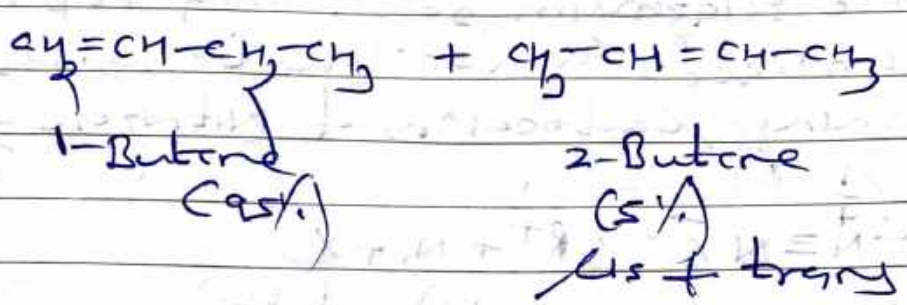


The pyrolysis of quaternary ammonium hydroxides to produce alkenes is called Hofmann Elimination Rxn.



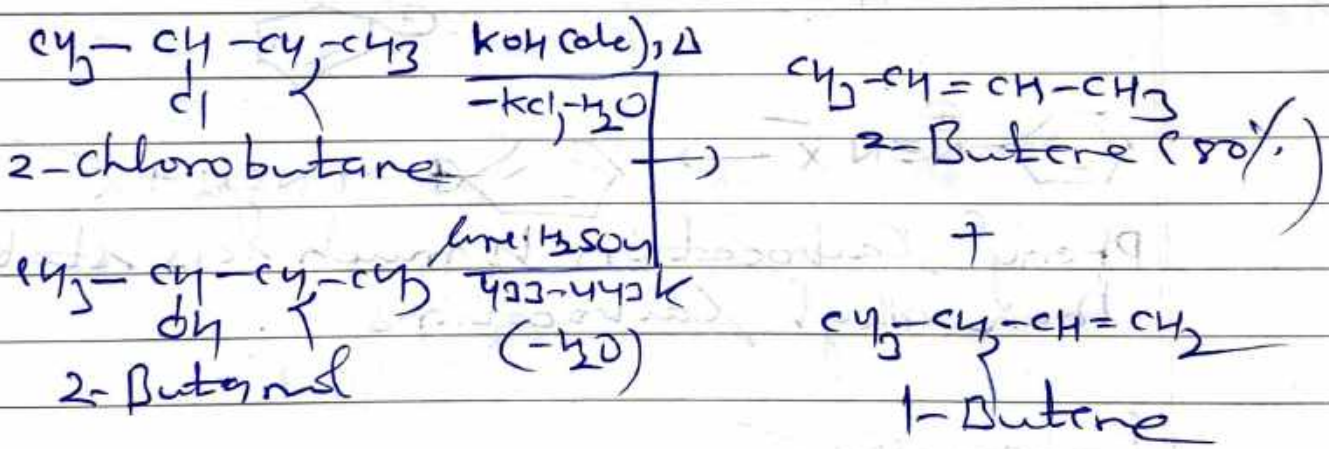
In Hofmann rxn, it is the less sterically hindered or more acidic β-hydrogen that is removed & hence in this rxn, less substituted alkenes are the major products





Saytzeff Elimination

It is a base catalysed dehydrohalogenation of alkyl halides & acid catalysed dehydration of alcohols, it is always the more highly substituted alkene that predominates



Diazonium Salts:

General formula: $ArN_2^+X^-$

$(-N^+\equiv N) \rightarrow N_2^+ \rightarrow$ diazo group

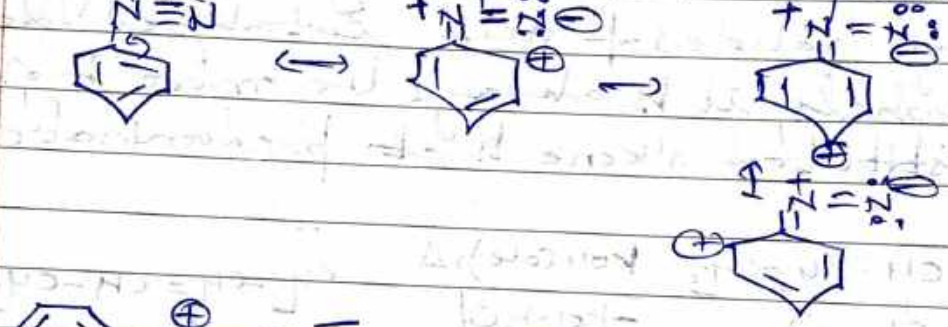
Stability of Diazonium Salts:

→ Primary aliphatic amines form highly unstable alkane diazonium salts. They rapidly decomposed even at low temp. (<273-278K) forming carbocations & Nitrogen gas.

$$R-\overset{+}{N}\equiv N\ \bar{X} \longrightarrow R^{+} + N_2 + X^{-}$$

(very stable)

→ Primary aromatic amines are stable for a short time at low temperatures (273-278K) It is due to dispersal of the positive charge



Phenyl carbocation is much less stable than alkyl carbocations

Preparation:

(1) from amines

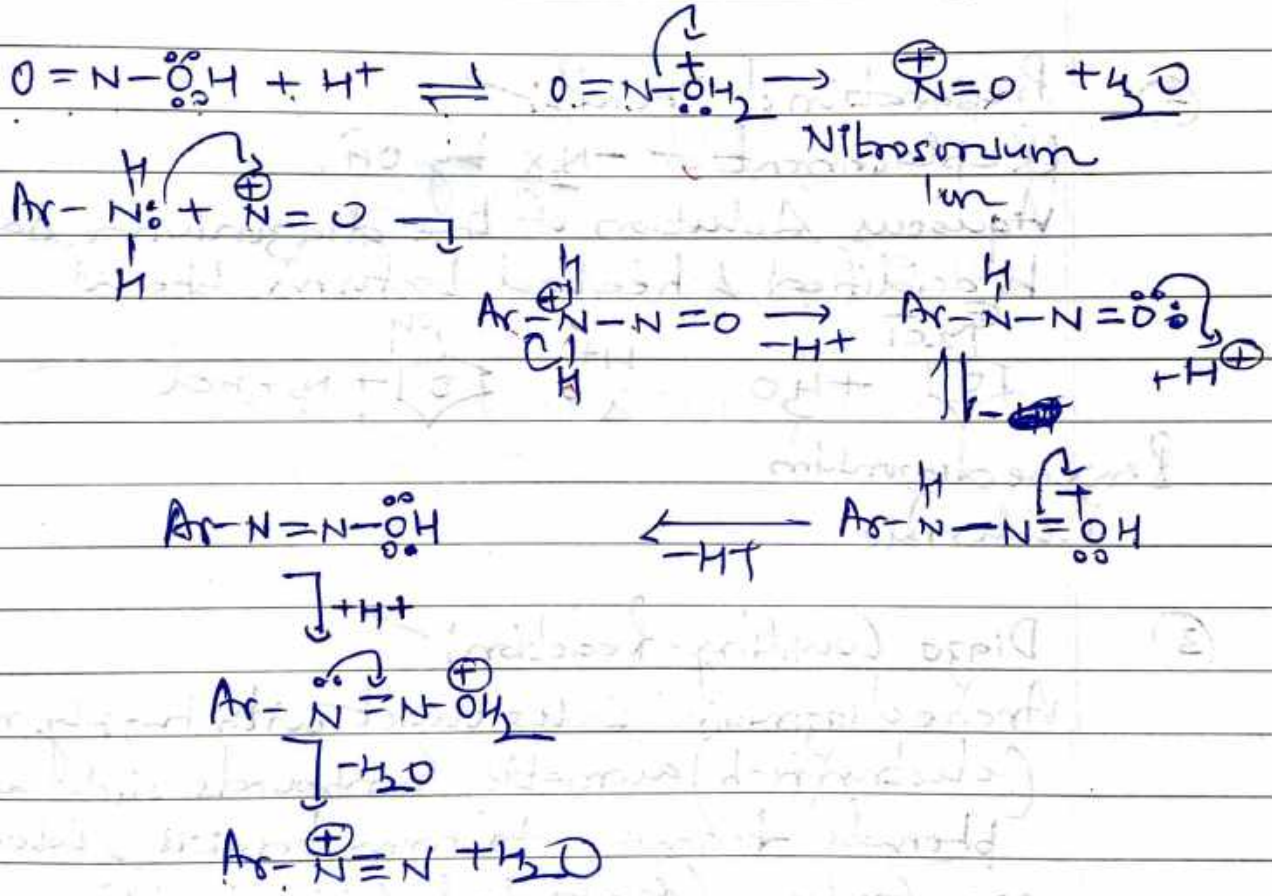
Aromatic diazonium salts are generally prepared by adding a cold aqueous soln of $NaNO_2$ to the soln of primary aromatic amines in an acid 273-278K.

$$ArNH_2 + NaNO_2 + 2HCl \xrightarrow{273-278K} ArN_2^{+}X^{-} + NaCl + 2H_2O$$

Eg: $C_6H_5NH_2 + NaNO_2 + 2HCl \xrightarrow{273-278K} C_6H_5N_2^+Cl^- + NaCl + 2H_2O$

This process of conversion of a primary aromatic amines into its diazonium salt is called diazotisation.

Mechanism,

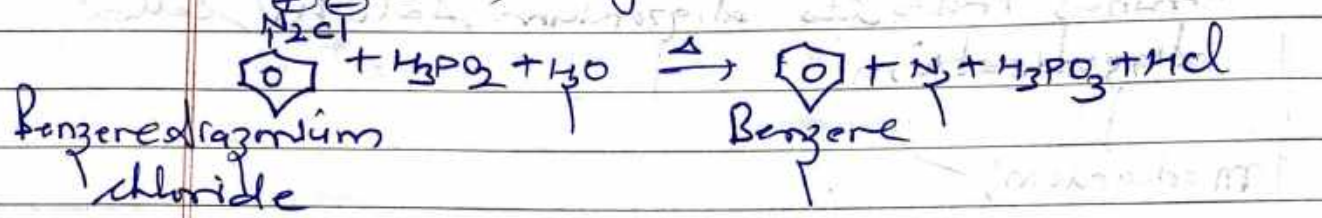


Evidence, aromatic amines containing electron withdrawing gps such as $-NO_2$ are less easy to diazotise.

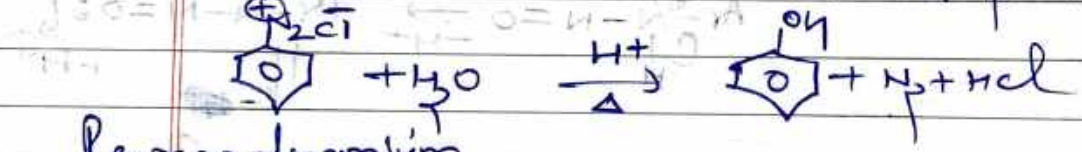
Page No.
Date:

Rxn Involved

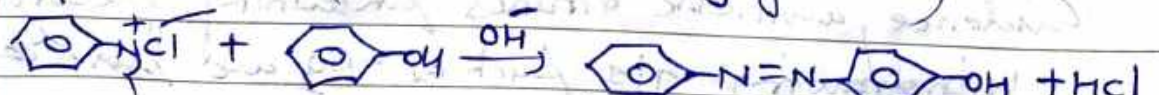
① Preparation of ~~amines~~ benzene:
Reduction to Arenes (Replacement of $-N_2X$ by H)
A diazonium salt is reduced by hypophosphorous acid (H_3PO_2) to give respective arene.

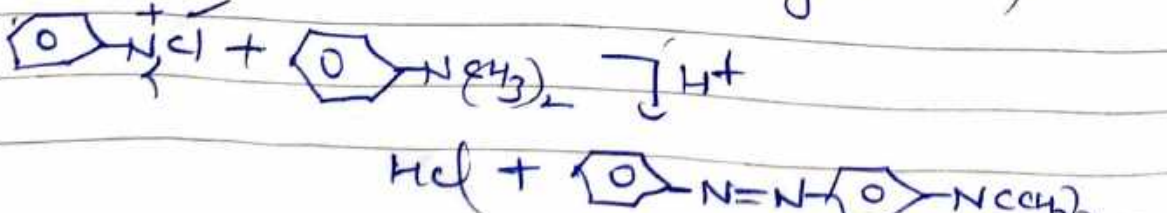


② Preparation of Phenol:
(Replacement of $-N_2X$ by OH)
Aqueous solution of the diazonium salt is acidified & heated to form phenol.



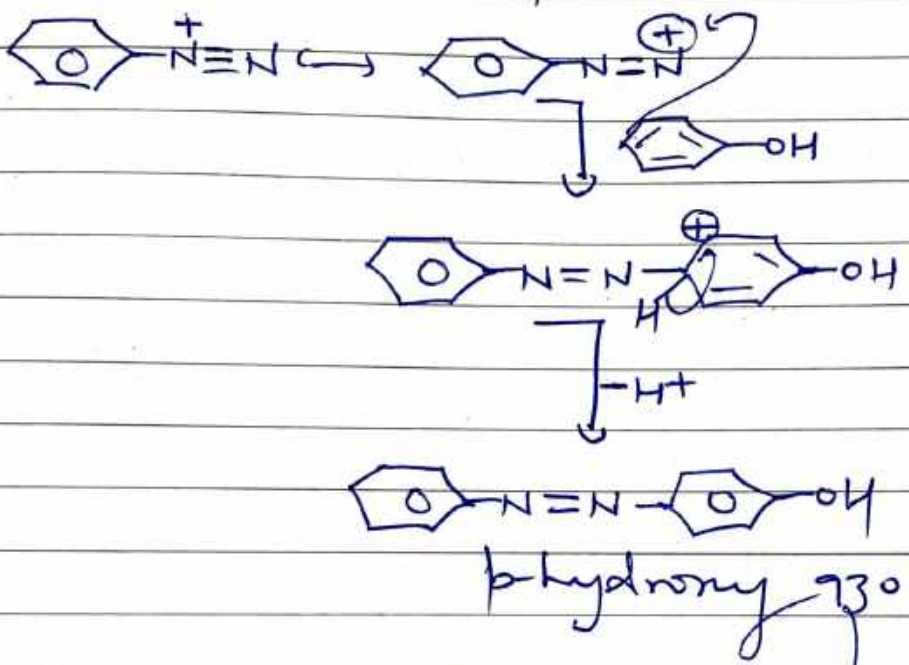
③ Diazo Coupling Reaction:
Arenediazonium salts react with highly reactive (electron rich) aromatic compounds such as phenols & amines to form brightly coloured azo compound (extended conjugated)





Such reactions in which the diazonium ion is coupled to the ring of phenol or amine is called Diazo Coupling Rxn.

mechanism: Electrophillic aromatic Substitution



p-hydroxy azobenzene

(if para position is blocked, it occurs at the Ortho position)