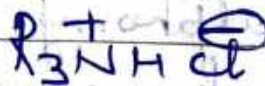
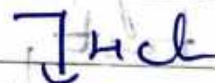


3° amine

No rxn, 3° amine insoluble in KOH



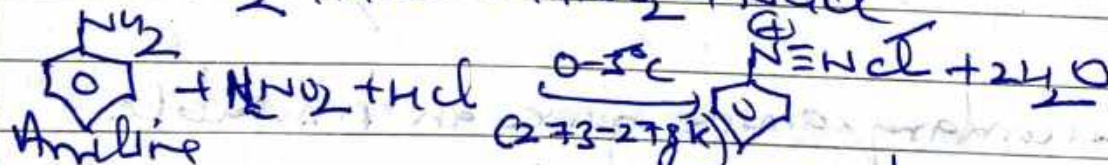
Soluble in HCl

③ Reaction with Nitrous acid:-

Primary, Secondary & tertiary amines react differently with nitrous acid. Since nitrous acid is unstable, it is prepared in situ by action of dil HCl acid on Sodium nitrite

a) Primary amines

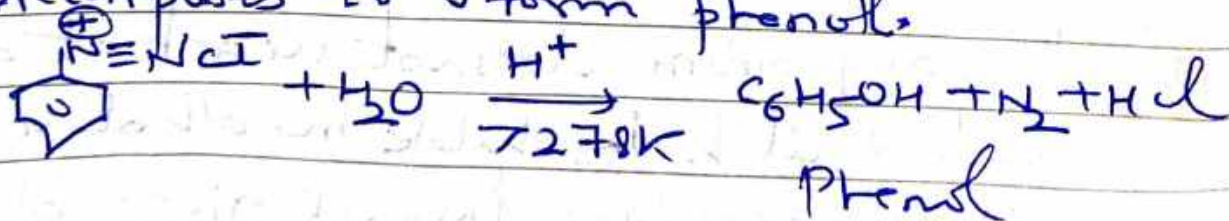
(i) Aromatic primary amines



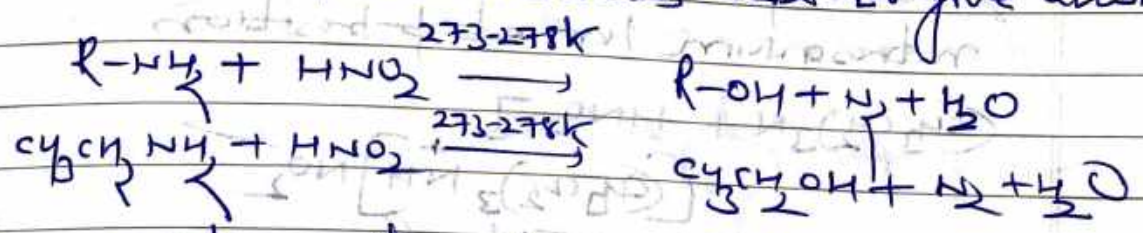
Benzene diazonium chloride

This rxn of converting aromatic primary amine into diazonium salt is called diazotisation rxn.

If however, the temperature rises above 278K, the initially formed diazonium salt decomposes to form phenol.

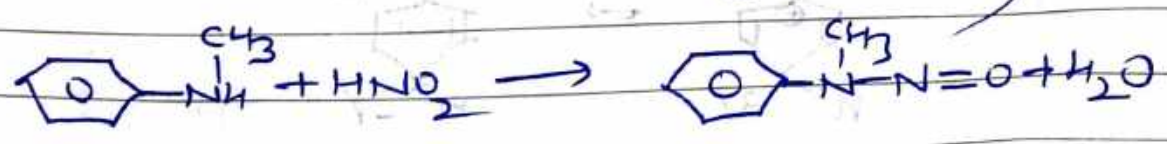
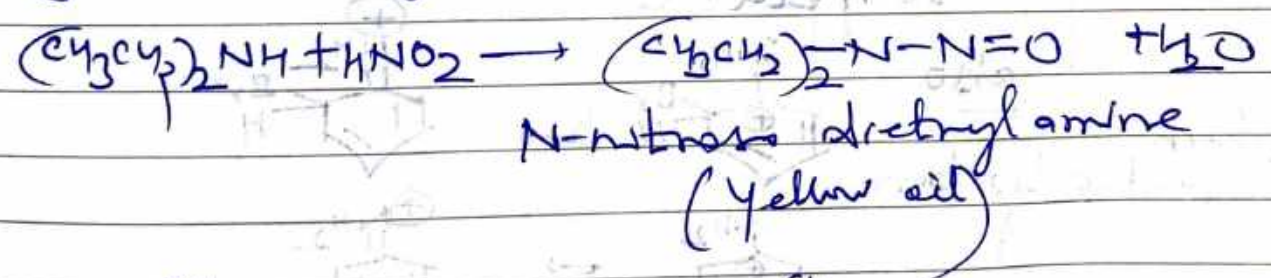


(ii) Aliphatic primary amines, on the other hand react with cold nitrous acid to give alcohols



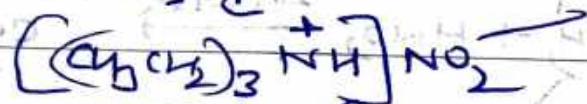
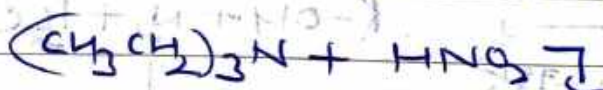
Since no other class of amines liberates N_2 gas on treatment with HNO_2 , this rxn is used as a test for aliphatic primary amines (primary aliphatic amines forms alkane diazonium salts with nitrous acid at $0-5^\circ C$ but they are not stable & decomposes to give alcohol & N_2)

b) Secondary amines
Both aliphatic & aromatic secondary amine on rxn with nitrous acid gives N-nitrosoamines which being insoluble in dil HCl separates as yellow oily compound

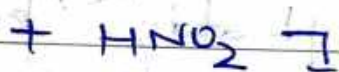


c) Tertiary amines
Tertiary aliphatic amines on rxn with HNO_2 form water soluble nitrite salt while

aromatic tertiary amines undergo electrophilic substitution with nitrosoum ion at p-position



Triethylammonium nitrite
(soluble)

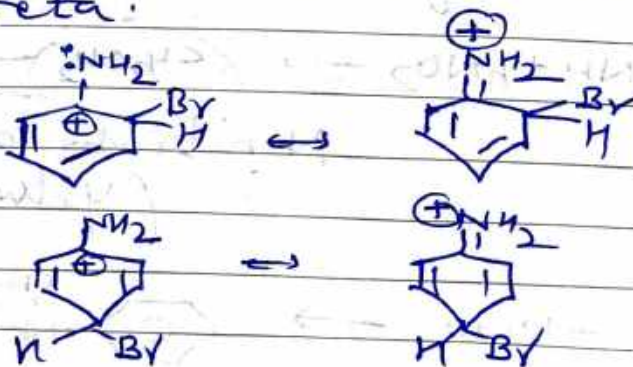


Electrophilic Substitution rxn of Aniline
(+R effect of $-\text{NH}_2$)

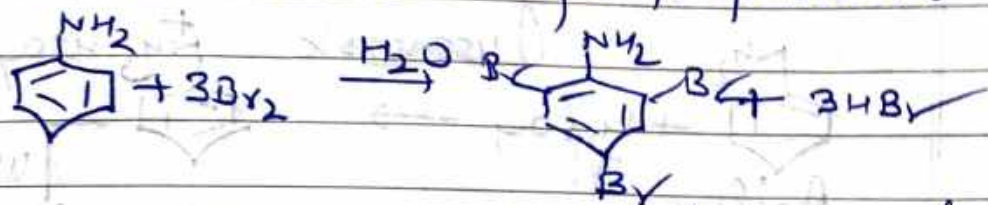
NH_2 strongly activates the aromatic ring through delocalization of the lone pair of electrons on the N-atom over the aromatic ring. As a result π density is more at o, + p-positions as compared to meta.

also

Such delocalization



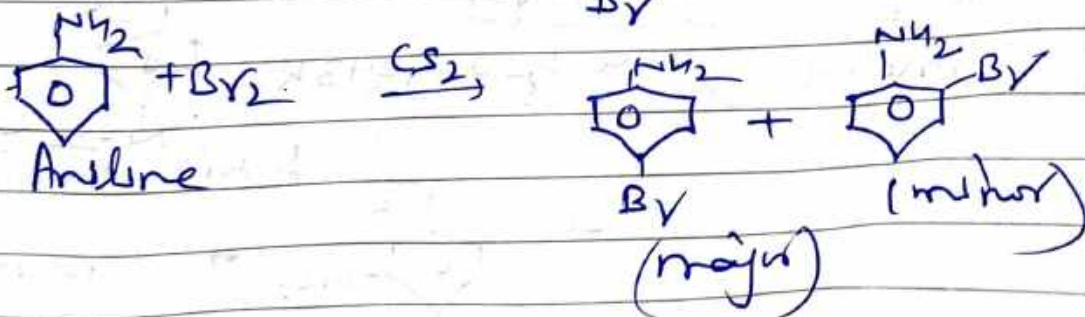
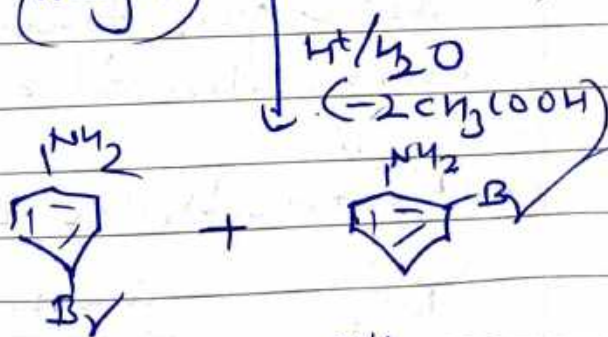
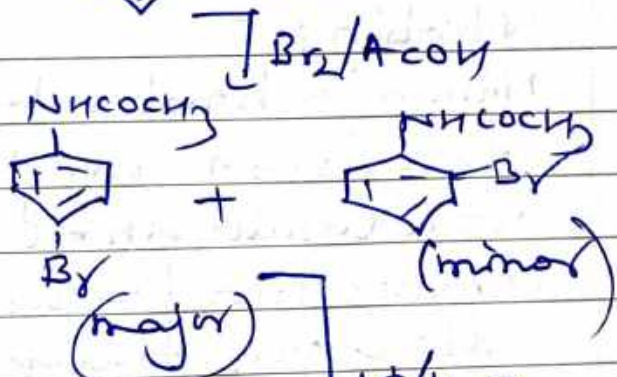
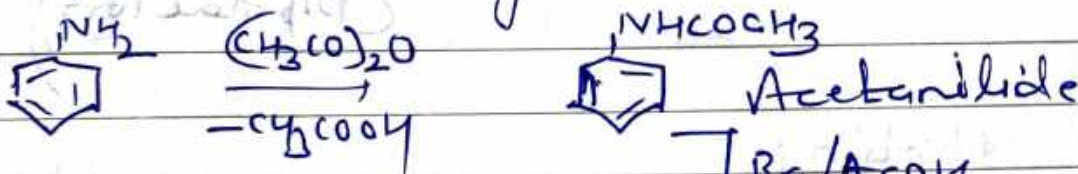
1) Halogenation :-
 Halogenation of amines occurs v. fast +
 halogen enters the o, + p positions



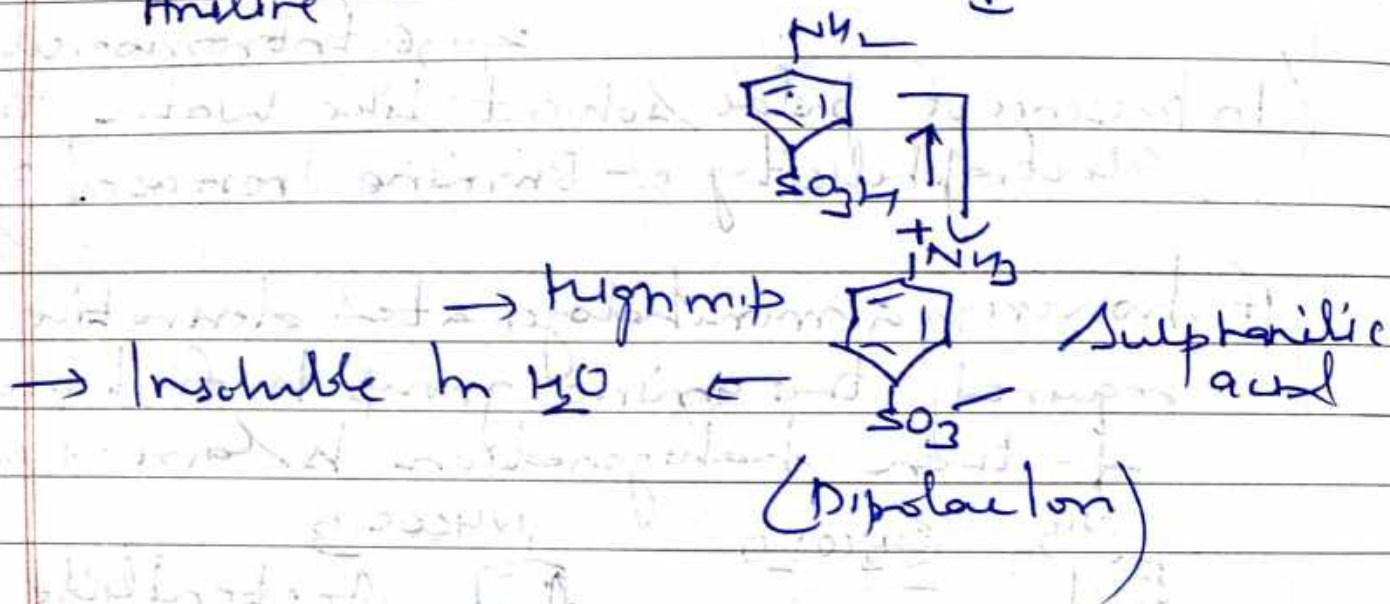
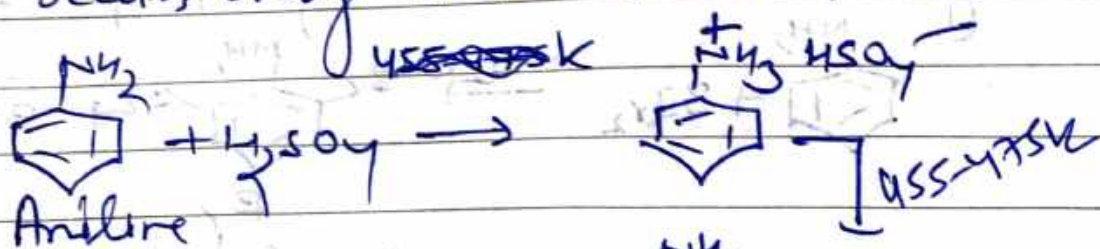
2,4,6-tribromoaniline

(In presence of polar solvent like water, the electrophilicity of Bromine increases)

If however, a monohalogenated derivative is required, the amino group is first acetylated + then halogenation is carried out.



ii) Sulphonation of aromatic amines occurs only under drastic conditions

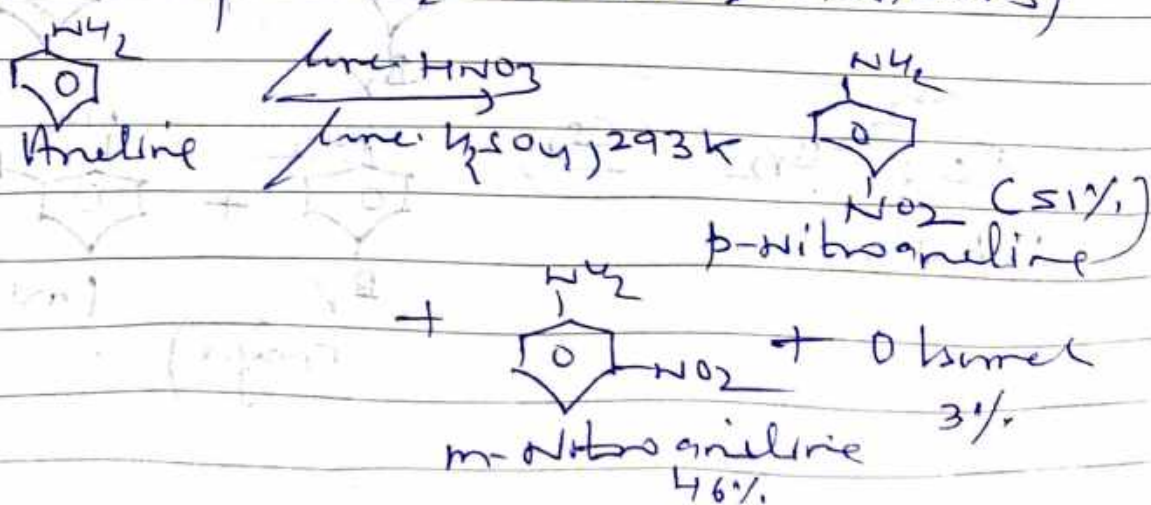


iii) Nitration:

Nitric acid is not only a nitrating agent but also acts as a strong oxidizing agent.

As a result, direct nitration of aromatic amines is not a useful rxn since it often gives tarry oxidⁿ products along with nitration products.

However, under controlled conditions,

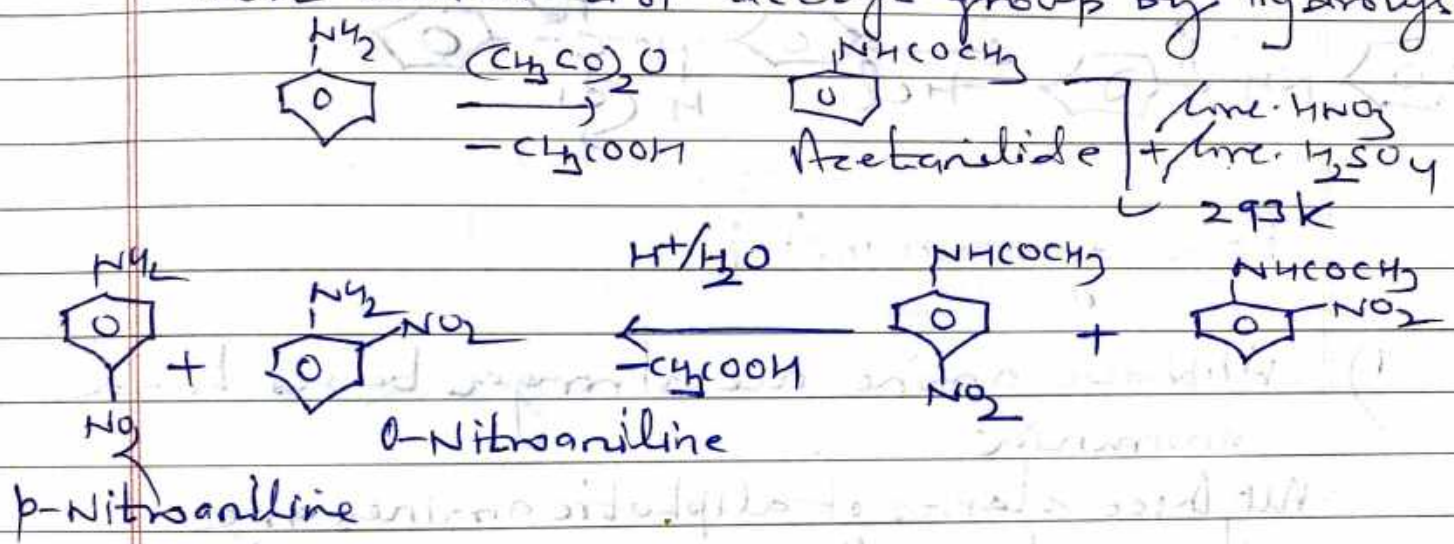


form of m-isomer:

In strongly acidic conditions, aniline is converted into anilinium ion since $-NH_3^+$ is a m directing group, therefore, an unexpected large amount of m-nitroaniline is obtained.

Efficient & 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.

