

Amines from NCERT and random notes i found online

July 4, 2025

Preparation of Amines:

- Reduction of Nitro compounds: When nitro compounds are reduced we get amines, they can be both benzylic and alkylic if that's a word
Fe + HCl is preferred mode of creating amines in these methods because it hydrolyses to release HCl during reaction in situ. Therefore fresh supply of HCl incoming all the time.
- Ammonolysis: As the name suggests, we break a bond with NH₃ molecule of RX and settle ourselves there at 373K. Because we formed a RNH₂ yet we can add more R's to it.. we do that and end up with $R_4N^+X^-$. Which is then turned into amine with the help of NaOH. The reaction for that is: $R_4N^+X^- + NaOH \longrightarrow 4RNH_2 + H_2O + NaX$. Which is great. Disadvantage of this is that we get a mix of all degree products which is difficult to separate. This is also not valid for aryl amine
- Reducing nitriles: Simply hydrogenation of C triple bond N.
- Reducing amides: Amide when reduced loses the carbonyl carbon entirely and the main carbon now has hydrogens to fill the valency.
- Gabriel phthalimide synthesis: We take RX and add some of that potassium phthalimide ion. This will create N-R group from N-K in the phthalimide ion.. now we add NaOH, which will cleave the bonds between carbonyl carbons and the nitrogen atom. Finally we are left with a RNH₂ and phthalimide ion which you may predict but having ONa instead of

H atoms. If I would put the bond cleavage part differently I would say.. "Two NaOH molecules break to give 2OH^- and 2H^+ which will then bond with the phthaline ion and the amine respectively" Aromatic primary amines cannot be prepared with this method because aryl halides do not undergo nucleophilic substitution.

- Hoffman bromamide degradation: It is used to prepare amines from amide using bromine gas in NaOH.. the end by products are Na_2CO_3 and NaBr along with water.
- Special reaction: alkylammonium salt is reacted with NaOH. This will give $\text{RNH}_2 + \text{NaX} + \text{H}_2\text{O}$

Chemical Properties of amine

- Friedel crafts alkylation: $\text{RNH}_2 + \text{CH}_3\text{Cl} \longrightarrow \text{R-NH-CH}_3 + \text{HCl}$
- Acylation: Primary amine with acid chloride gives amide and HCl molecule Similarly when we add secondary amine to acid anhydride we get carboxylic acid and amide.
- Benzoylation: Reaction of amine with benzoyl chloride at room temperature.
- Carbylamine reaction: It is used to test for primary amine where the amine is reacted with chloroform and base to form isocyanide foul smell It may also be used to distinguish between CCl_4 and CHCl_3 .. as both are very similar to each other. The reaction mechanism is that: CHCl_3 loses its H to OH^- and forms CCl_3^- which will form dichlorocarbene. This dichlorocarbene attacks the amine and creates the isocyanide with steps I do not know about.
- reaction with nitrous acid: Aniline can form diazonium salt. This salt when hydrolysed is converted to phenol and releases N_2 gas
- Hinsberg reagent: Test for primary amine. When primary amine reacts with Hinsberg reagent (it is PhSO_2Cl) also called benzene sulphonyl chloride, the sulphur atom breaks bond with Cl to remake it with the Nitrogen atom of amine which has now lost a hydrogen. This new thing

is now added to alkali and we find it to be soluble in it..(because there is a alpha H for making salt) Secondary amine does react but due to lack of alpha hydrogen atom it fails to be soluble. Tertiary amine does not give reaction.

- Bromination of Aniline: When aniline is brominated, it over brominates and forms a white ppt of 2,4,6-tribromoaniline changing the colour from reddish brown to white. To prevent this thing from happening we will do acetylation of the nitrogen group(essentially adding a EWG.) And remove the same after our bromine is added by hydrolysis.
- Nitration of aniline: Before the nitration even takes place using the concH₂SO₄ and concHNO₃, we get a anilinium ion on the ring. This anilinium ion now in its ortho and para products of NO₂ is stabler in the para one.. because when in ortho i dont know the reason.
- Sulphonation of aniline: When aniline is reacted with concH₂SO₄ we get a salt with $NH_3^+SO_4^-$ which at high temperature breaks down to get us para and ortho "4-paranitro sulphonic acid which also behaves as a zwitter ion.
- Why aniline cannot give friedel crafts reaction? Because when it tries to do that.. the strong lewis acid AlCl₃ ends up reacting with the lone pair of nitrogen on aniline instead.
- Smaller the size more the solvation.
- Chemical prop of Diazonium: 1. N_2Cl^- can be replaced with Cl or Br by adding HX.2. Replace with CN by adding HCN.3. Replace by OH by adding water.4. Replace with H by adding H₃PO₂.5. Replace with F by adding HBF₄.6. Replace with I by adding KI.6. Replacement by NO₂ can be done by adding HBF₄ and then NaNO₂ so that in the end only NO₂ is there. with by products being the NaBF₄ and HCl.
- Coupling reaction of azo dye test: benzene diazonium salt is taken with a electron donating group based aromatic compound.. and this compound will lose its para hydrogen to the Cl- of the diazonium to produce HCl and another compound as a result of both nitrogen atoms being distributed between the two aromatic compounds with a double bond in between.

- can be replaced by COOH but don't add CH₃COOH directly to diazonium that won't do anything.
- Most conversions start with NO₂ which is then converted to NH₂ and then we can easily create diazonium and get other substituents
- Do the benzoic acid to aniline conversion
- $\text{CH}_3\text{NH}_2 \xrightarrow{\text{HNO}_2 \text{ and } \text{HCl}} \text{CH}_3\text{OH}$
- To reduce carbon atom: Hofmann bromamide degradation (remove a C=O whole)