

1- Chapter 22: Amines

- *Amine Nomenclature (section 22.1, slides 3-8):* Recognize whether an amine is primary ($R-NH_2$), secondary (R_2NH) or tertiary (R_3N). Know what an aniline is (amino-substituted benzene). Recognize and understand that amines are pretty good nucleophiles, better than alcohols (remember imine and enamine formation from aldehydes and ketones, amide formation from acyl electrophiles, etc.); this is due to the fact that nitrogen is less electronegative than oxygen, more willing to share its electron pair (see resonance stabilization in amides for example). Know how to name amines from IUPAC rules: 'alkylamine', 'dialkylamine' and 'trialkylamine' for primary, secondary, tertiary amines respectively when all R groups are the same. When not the same, find the R group with highest priority (the parent primary amine, with longest or cyclic R group) and follow this format: *N-alkyl(1)alkyl(2)amine*, where *alkyl(2)amine* is the parent primary amine with highest priority (secondary amines) OR *N-alkyl(1)alkyl(2)alkyl(3)amine*, where *alkyl(3)amine* is the parent primary amine with highest priority (tertiary amines).
- *Basicity of Amines (section 22.4, slides 10-13):* Understand that amines are relatively good bases. Know the approximate pK_a of the corresponding conjugate acids (ammoniums): around 10-11 for alkyl amines, around 5 for most aniline derivatives; understand with resonance forms why there is such a big difference between alkyl amines and aniline derivatives.
- *Formation of Amines (section 22.7-22.10, slides 15-25):* Understand that alkyl amines cannot be cleanly synthesized using simple S_N2 displacement of ammonia with alkyl halides, due to multiple alkylations; the more substituted the amine is, the more nucleophilic it is, so it is difficult to stop after only one S_N2 . For this reason, other methods have been developed to circumvent this problem:
 - (1) Gabriel amine synthesis (slides 16-18): good only for primary amine synthesis, know the conditions seen in class including NH_2-NH_2 for the phthalimide removal (know what a phthalimide is); no need to know the mechanism for the phthalimide removal step.
 - (2) reduction of CN to CH_2NH_2 with $LiAlH_4$ (simply know the conditions, not the mechanism, slide 19-20): only good for primary amine synthesis;
 - (3) reduction of amides ($C(O)NR_2$ to CH_2NR_2 with $LiAlH_4$ (simply know the conditions, not the mechanism, slide 19-20): good for primary, secondary and tertiary amine synthesis depending on the amide substrate (e.g. a secondary amide substrate will give a secondary amine product);
 - (4) Reductive amination from amines and aldehydes/ketones with $NaBH_3CN$ (know the conditions and the mechanism, slide 19 and 21-22): good for primary, secondary and tertiary amine synthesis depending on amine substrate (e.g. secondary amine substrate will give a tertiary amine product). The most versatile method for amine synthesis.
 - (5) Reduction of azides with $LiAlH_4$ (simply know the conditions, not the mechanism, slide 19 and 23): only good for primary amine synthesis, very practical when starting from an alkyl halide (S_N2 displacement with NaN_3 , then reduction to primary amine with $LiAlH_4$).
 - (6) Reduction of nitro groups with H_2/Ni OR Fe/HCl (simply know the conditions, not the mechanism, slide 19 and 23): only good for primary amine synthesis, very practical for the synthesis of anilines (Nitration of arene with HNO_3/H_2SO_4 , then reduction with either H_2/Ni or Fe/HCl).Be able to use these different methods for the synthesis of various amines (see retrosynthesis on slides 24-25)

Organic Chem Amine Study Guide

Christian G. Meyer



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