



nitrogen's lone pair makes every amine a base and a nucleophile, but steric bulk and solvation decide how strong

Classification of amines

Aliphatic amine

- N attached to sp^3 alkyl carbon(s)
- 1° $R-NH_2$, 2° R_2NH , 3° R_3N , classified by carbons ON nitrogen, not the carbon skeleton
- N lone pair sits free, not conjugated anywhere

Aromatic amine

- N attached directly to the aromatic ring, e.g. aniline
- same 1°/2°/3° naming, but the N lone pair conjugates into the ring
- delocalisation makes this lone pair less available, so the ring-attached N is a weaker base

amine classification counts carbons ON THE NITROGEN, unlike alcohol/halide classification which counts carbons on the functional carbon. This trips up almost everyone the first time

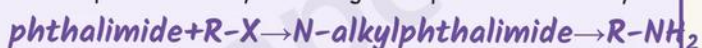
Structure of the amine nitrogen

- nitrogen is sp^3 hybridised with a pyramidal shape, the lone pair occupying the fourth position
- aromatic amine's N flattens toward sp^2 so its lone pair aligns with the ring's pi system
- this lone pair makes every amine both a Lewis base (donates it) and a nucleophile

count the carbons ON nitrogen, not around it, that single habit fixes almost every classification mistake in this chapter

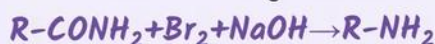
Preparation of amines

Gabriel phthalimide synthesis: gives a pure 1° amine only



reduction of a nitrile $R-CN + H_2 \rightarrow R-CH_2NH_2$

Hofmann bromamide degradation: one carbon shorter



then hydrolysis



Gabriel synthesis: alkylation of the phthalimide anion, later hydrolysed to release a pure primary amine with no over-alkylation

Gabriel synthesis cannot make an aromatic amine, since aryl halides do not undergo the needed SN_2 step with the phthalimide anion

Basicity of amines: the counterintuitive order



- in the gas phase, basicity is $3^\circ > 2^\circ > 1^\circ > NH_3$: alkyl groups donate, freeing the lone pair
- in water (the order actually tested), sterics and solvation flip this: simple alkyl amines run $2^\circ > 1^\circ > 3^\circ > NH_3$
- reason: 3° 's cation solvates worst (fewest N-H bonds for water), so LESS stable despite most donation
- aniline's basicity is far lower than ammonia or any aliphatic amine: lone pair tied in ring conjugation

