

9.6 Chemical Reactions of Amines

⚡ High

Structural relationships, basicity trends,
and definitive diagnostic tests.

The Math of Basicity

Formula Callout

$$K_b = \frac{[R-NH_3^+][OH^-]}{[R-NH_2]}$$

$$pK_b = -\log K_b$$

The Golden Rule

Higher $K_b \rightarrow$ Lower $pK_b \rightarrow$ Stronger Base

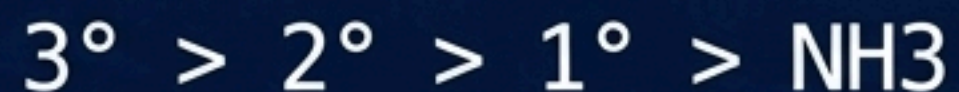
pKb Values in Aqueous Phase

Group	pKb Range	Diagnostic
Aliphatic Amines	3.00 - 4.22	Strong Base
Ammonia	4.75	Weak Base
Aromatic Amines	8.92 - 9.38	Weak Base

The Phase Dependency of Basicity

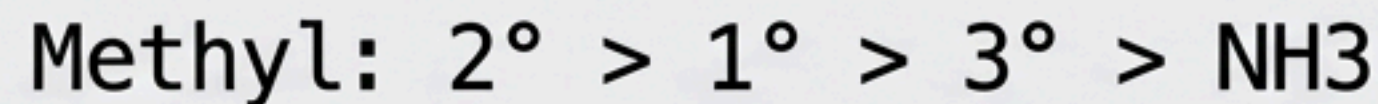
Gas Phase

Trend follows Inductive Effect strictly.



Aqueous Phase

Trend blends Inductive + Solvation + Steric effects.





You've Learned the Theory. Let's Test Them Now.

$$E=mc^2$$



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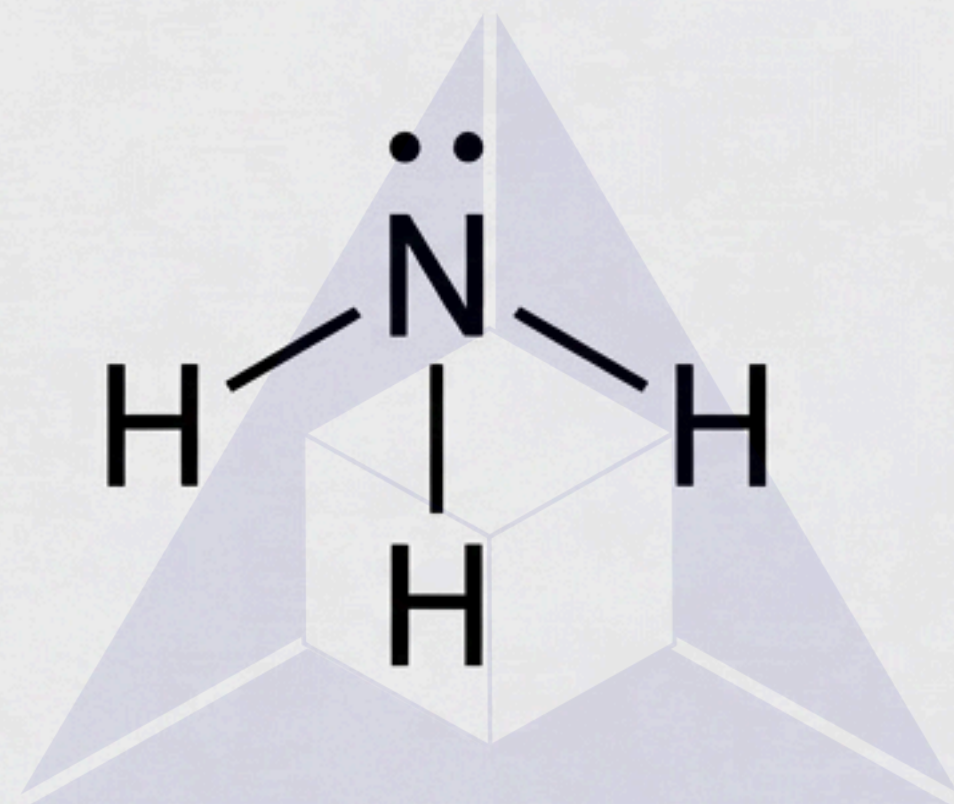
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Key Highlights

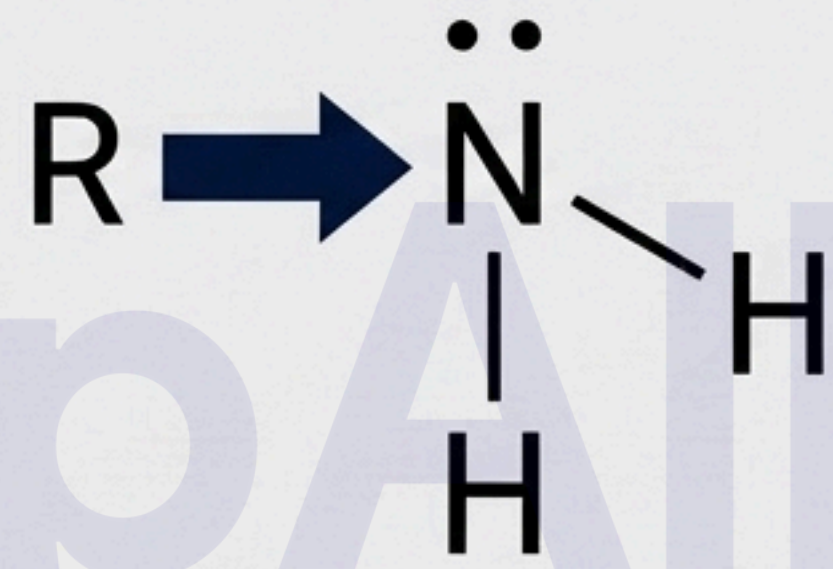
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The +I Effect in Action



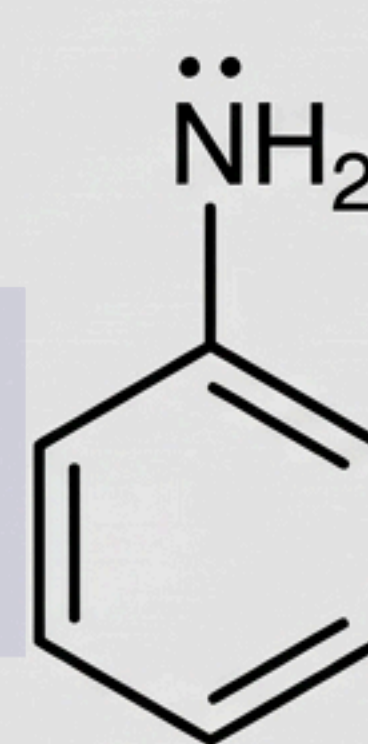
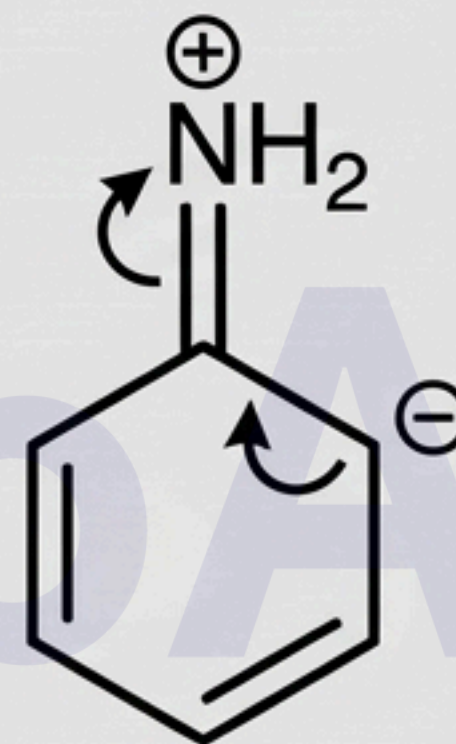
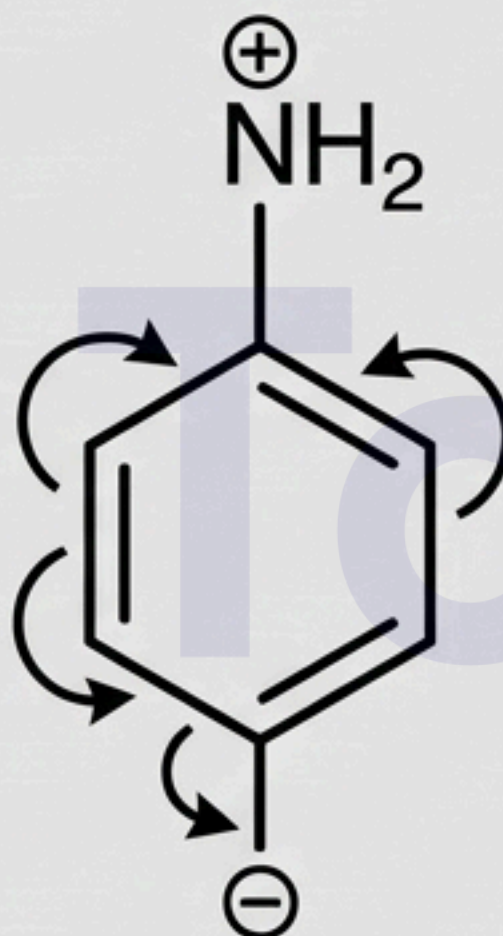
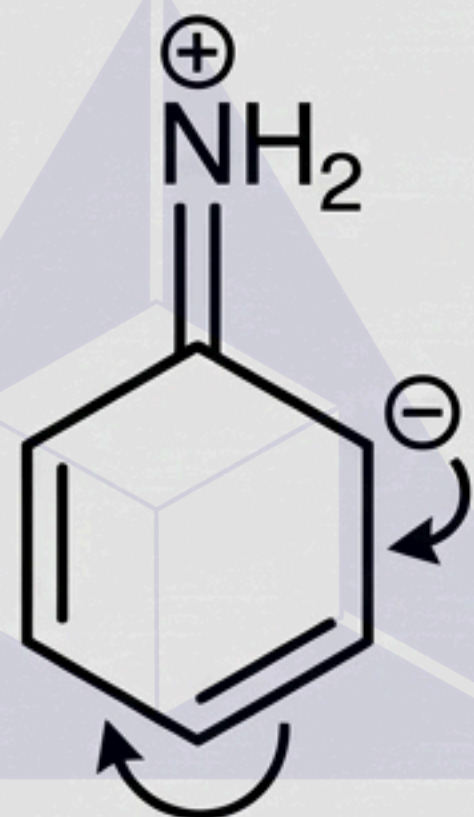
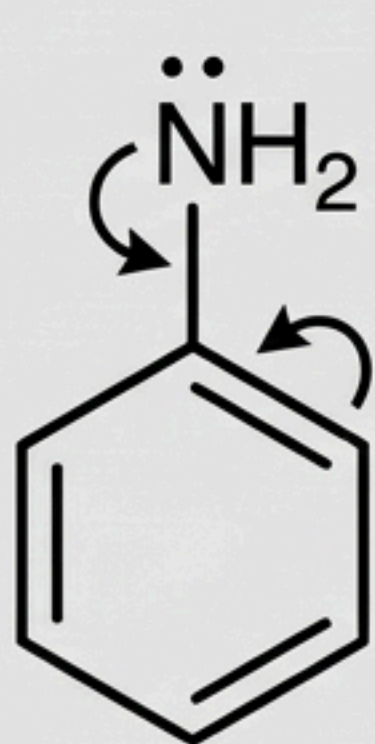
Ammonia (Baseline)



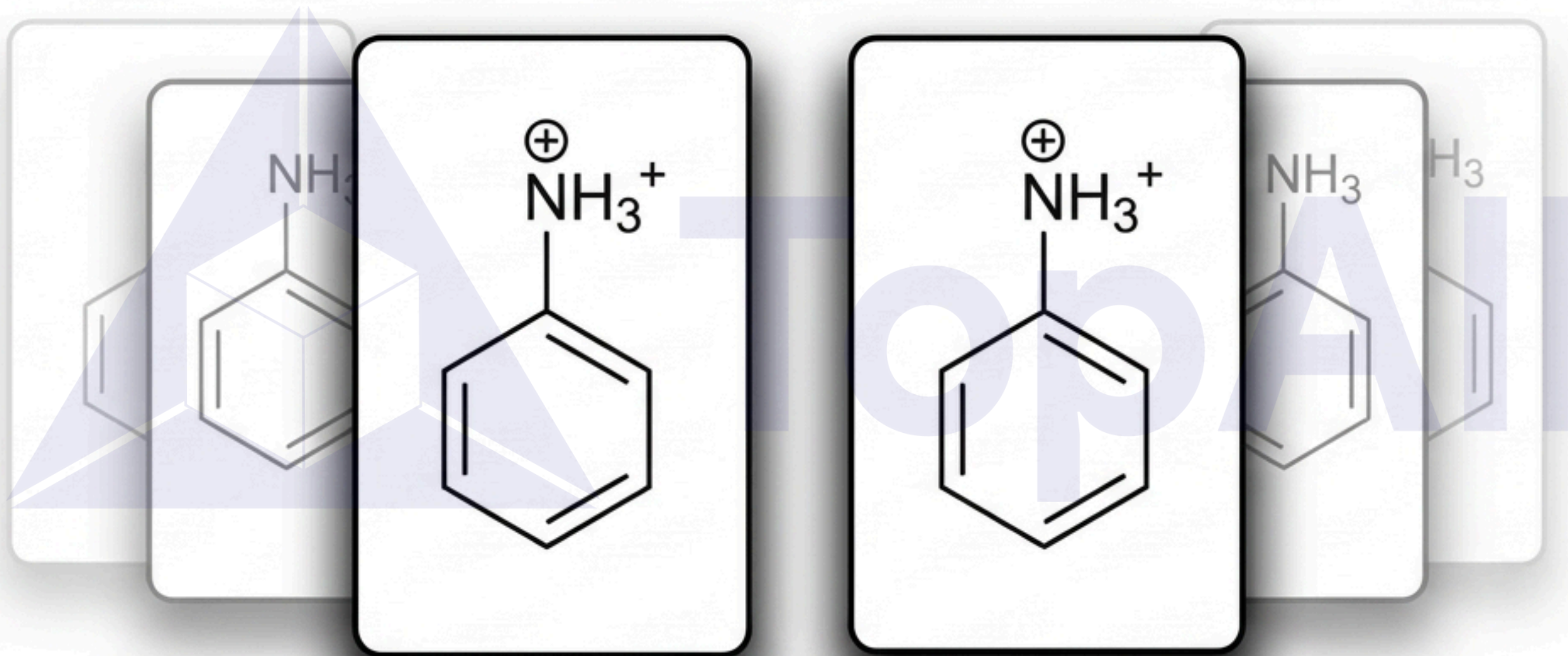
Alkanamine (+I Effect)

Alkyl groups push electron density toward nitrogen (+I effect). This makes the unshared pair more available for protonation and stabilizes the substituted ammonium ion.

Why Aniline is Exceptionally Stable



Protonation Destroys Resonance

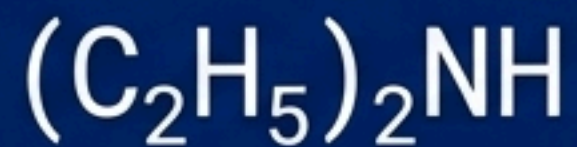


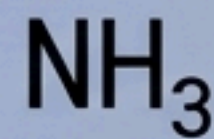
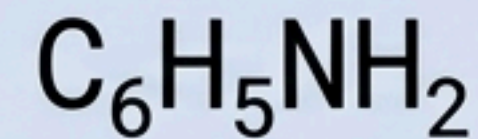
Structure-Basicity Synthesis & Ranking

Aniline is less basic than ammonia because its lone pair is delocalized into the benzene ring (5 structures). Protonation forms an anilinium ion restricted to only 2 structures.

More stable reactant = weaker base.

Example 9.4


$$>$$

$$>$$

$$>$$


Alkylation & Acylation

Alkylation

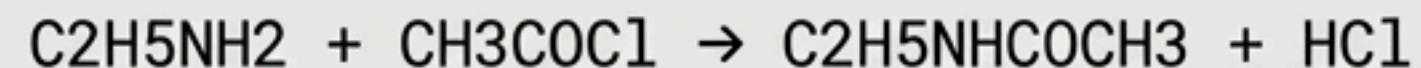
Amines + Alkyl Halides (RX)

→ Secondary, Tertiary, and Quaternary Ammonium Salts.

Acylation

Aliphatic/Aromatic (1° & 2°)
+ Acid Chlorides/Anhydrides

→ Amides.



The Carbylamine Reaction (Isocyanide Test)

Watch for this: **Strictly for 1° Amines only** (Aliphatic and Aromatic).
2° and 3° amines DO NOT react.

Condition: Heating with
Chloroform (CHCl₃) + Ethanolic
KOH.

Forms **isocyanides/carbylamines**,
producing a highly characteristic,
incredibly foul smell.



Hinsberg Test: Distinguishing 1°, 2°, 3° Amines

Reagent: Benzenesulphonyl chloride ($\text{C}_6\text{H}_5\text{SO}_2\text{Cl}$)

1° Amine → Forms Sulphonamide with an acidic H → **Soluble in alkali**



2° Amine → Forms Sulphonamide with NO acidic H → **Insoluble in alkali**



3° Amine → **No Reaction**



You've Learned the Theory.

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Practice the moment you finish studying
Jump in while the concept is still fresh in your head

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Electrophilic Substitution of Aniline

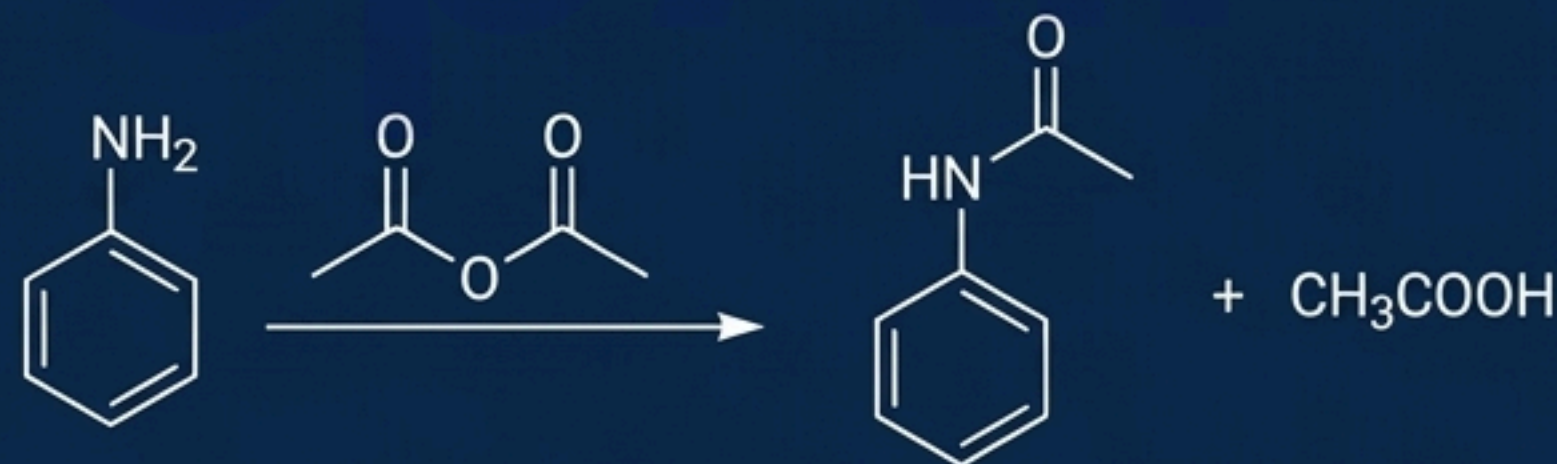
Bromination → Yields 2,4,6-tribromoaniline (white precipitate).

Nitration → Yields significant meta-derivative due to formation of the meta-directing anilinium ion in acidic medium.

Sulphonation → Yields a zwitterion (sulphanilic acid).

The Acetylation Trick

Aniline is dangerously reactive. Protect the highly activating -NH₂ group using acetic anhydride to ensure monosubstitution (para major), then hydrolyze back to an amine.



Module Synthesis

1. **Basicity Rules:** K_b and pK_b are inverted. Aliphatic amines $>$ NH_3 $>$ Aromatic amines.
2. **Phase Matters:** Solvation and steric hindrance scramble the basicity order in aqueous solutions.
3. **Diagnostic Tests:** Carbylamine = 1° only. Hinsberg = Separates 1° , 2° , 3° based on alkali solubility.

Try 9.7 Diazonium Salt Preparation next →