

UNIT 9 • AMINES

9.4 Preparation of Amines



High JEE Weightage



1. Nitro Compounds

$\text{H}_2/\text{Ni-Pd-Pt}$ or
 $\text{Fe}+\text{HCl}$

[See Reaction →](#)



2. Ammonolysis

Sealed tube 373K

[See Reaction →](#)



3. Nitriles

LiAlH_4 (Ascent of series)

[See Reaction →](#)



4. Amides

LiAlH_4 / H_2O

[See Reaction →](#)



5. Gabriel Synthesis

Phthalimide + KOH

[See Reaction →](#)



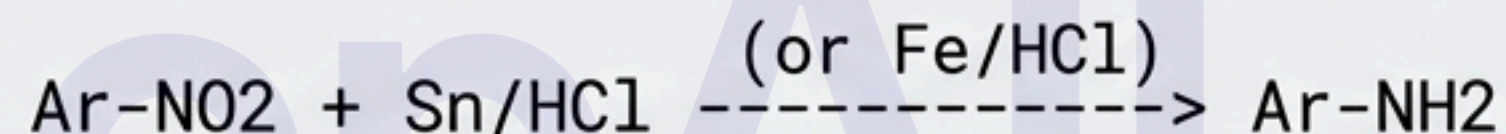
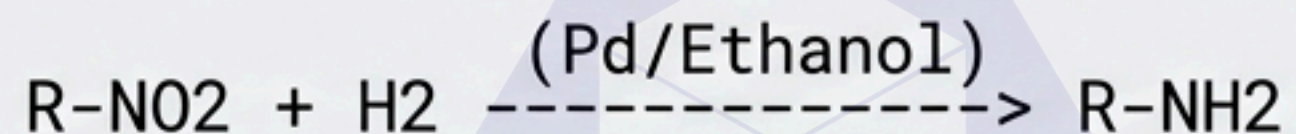
6. Hoffmann Bromamide

Br_2/NaOH (Descent)

[See Reaction →](#)

1. Reduction of Nitro Compounds

Nitroalkanes and nitroarenes are reduced to amines by passing hydrogen gas over finely divided catalysts or by reduction with metals in acidic mediums.



Why is Fe + HCl preferred?

FeCl₂ formed during the reaction gets hydrolysed to release continuous HCl. You only need a tiny initial amount of acid to initiate the reaction!



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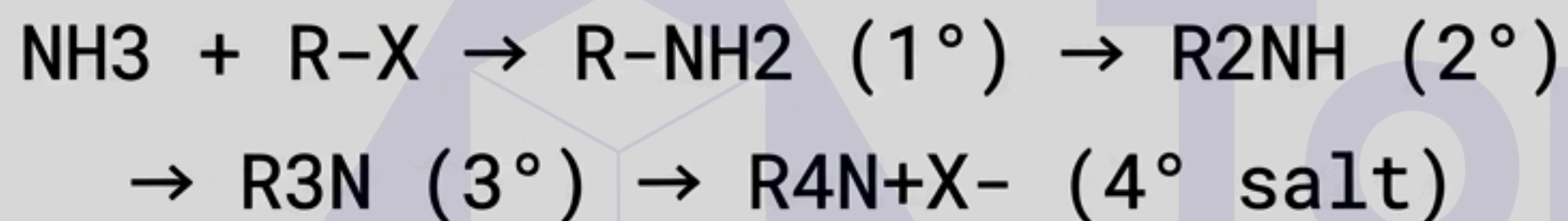
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2. Ammonolysis (Nucleophilic Substitution)

Condition: Ethanolic NH_3 in a sealed tube at 373K.
Cleavage of the C-X bond by an ammonia nucleophile.



- Reactivity Order: $\text{RI} > \text{RBr} > \text{RCI}$
- Freeing the amine:
 $\text{R-NH}_3^+ \text{X}^- + \text{NaOH} \rightarrow \text{R-NH}_2 + \text{H}_2\text{O} + \text{NaX}$

Watch for this mixture

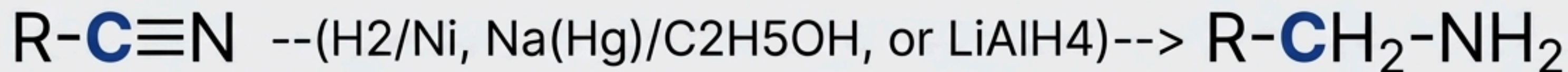
Ammonolysis naturally yields a messy mixture of 1°, 2°, 3° amines and 4° salts.

How to get 1° major?
Use a large excess of NH_3 .

3. Reduction of Nitriles

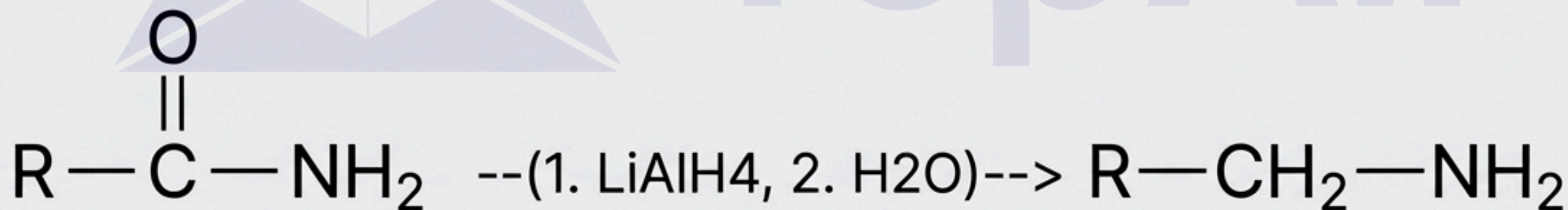
Ascent of Amine Series (+1 Carbon)

Used for preparing amines containing one carbon atom more than the starting amine. Crucial for step-up conversions in synthetic pathways.



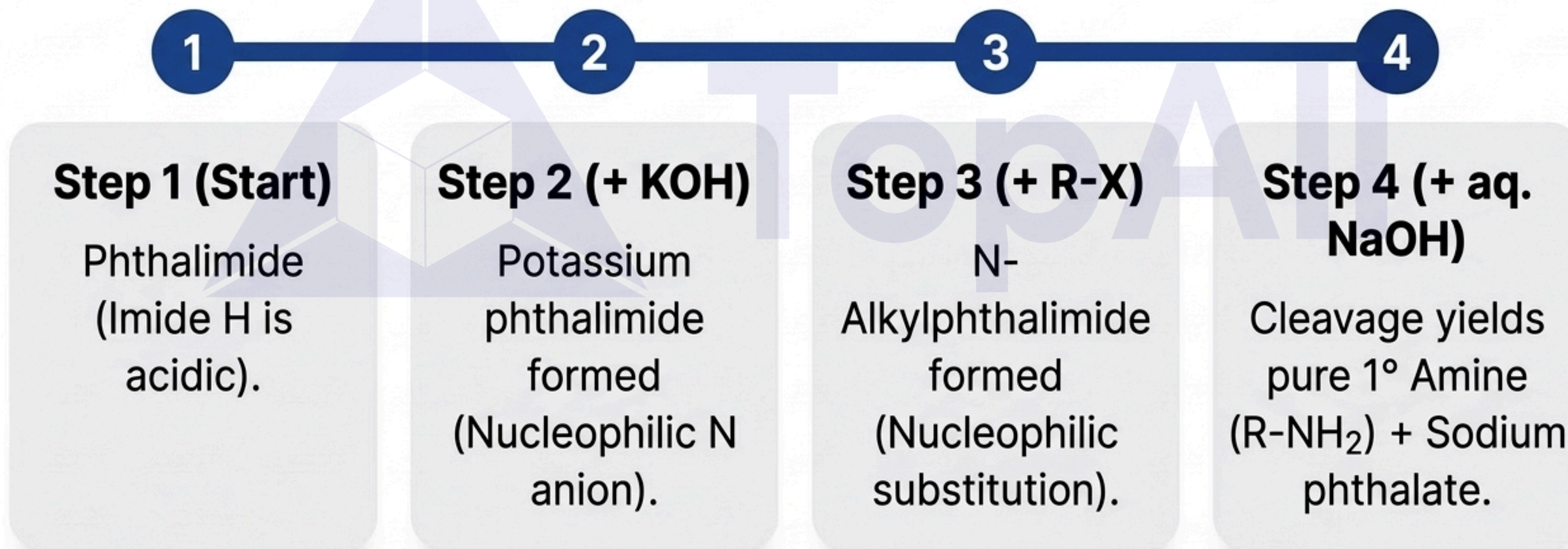
4. Reduction of Amides

Direct reduction of the carbonyl group of an amide into a methylene (-CH₂-) group using a strong reducing agent. The overall carbon count remains unchanged.



5. Gabriel Phthalimide Synthesis

The definitive method for pure primary aliphatic amines.





! JEE Trap: Can Gabriel synthesis make Aniline?

No. Aromatic primary amines cannot be prepared by this method.

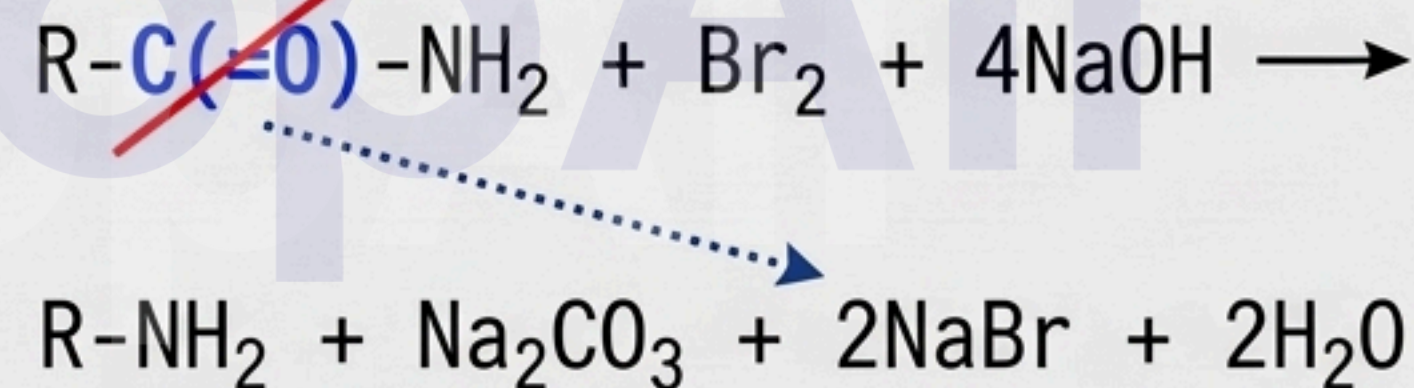
Why? The reaction relies on the nucleophilic substitution of an alkyl halide ($R-X$) by the bulky phthalimide anion.

The Catch: Aryl halides ($Ar-X$, like chlorobenzene) do not undergo nucleophilic substitution easily with the phthalimide anion due to the partial double bond character of the $C-X$ bond and intense steric/electronic repulsion.

6. Hoffmann Bromamide Degradation

One Carbon Less (Descent of Series)

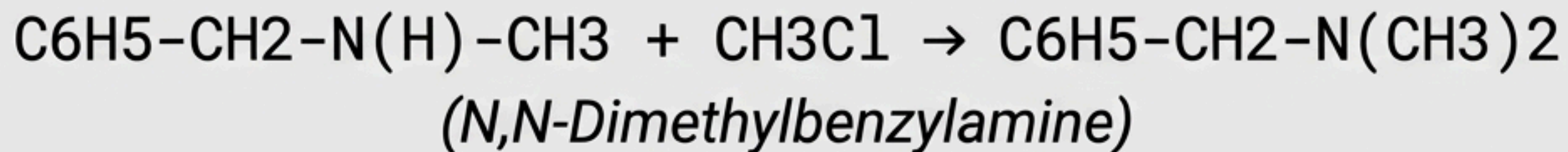
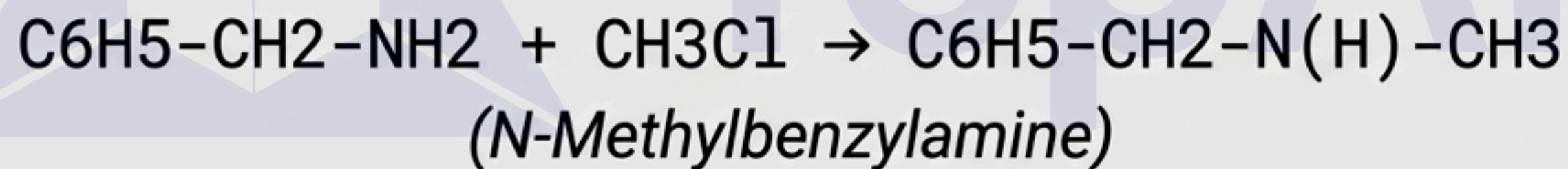
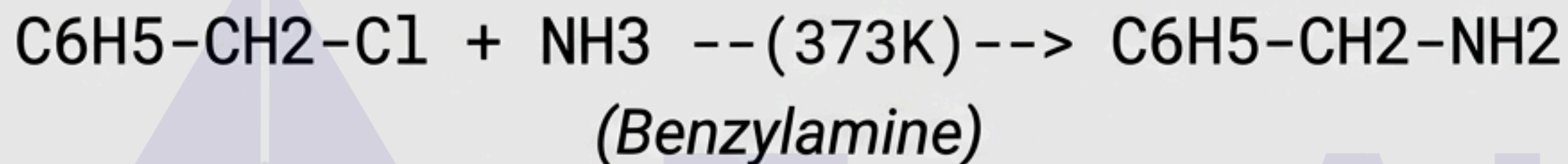
Migration of an alkyl/aryl group from the carbonyl carbon to the nitrogen atom. The resulting amine has one less carbon than the parent amide.



Worked Example: Ammonolysis & Alkylation (Ex 9.1)



Prompt: Ammonolysis of benzyl chloride, followed by reaction with 2 moles of CH_3Cl .



Concept Synthesis

- The Baseline: Reduction of nitro compounds, nitriles, and amides directly yield amines using standard reducing agents (H_2/Pd , LiAlH_4).
- The Chain Builders: Nitrile reduction adds a carbon (ascent of series); Hoffmann degradation removes a carbon (descent of series).
- The Mixture Problem: Ammonolysis yields a messy mixture of 1° , 2° , 3° amines unless excess NH_3 is used.
- The Pure Aliphatic Champion: Gabriel synthesis yields pure 1° aliphatic amines, but fails entirely for aromatic amines (cannot make aniline).



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