

UNIT 9 • AMINES

9.6.5 Electrophilic Substitution in Aniline



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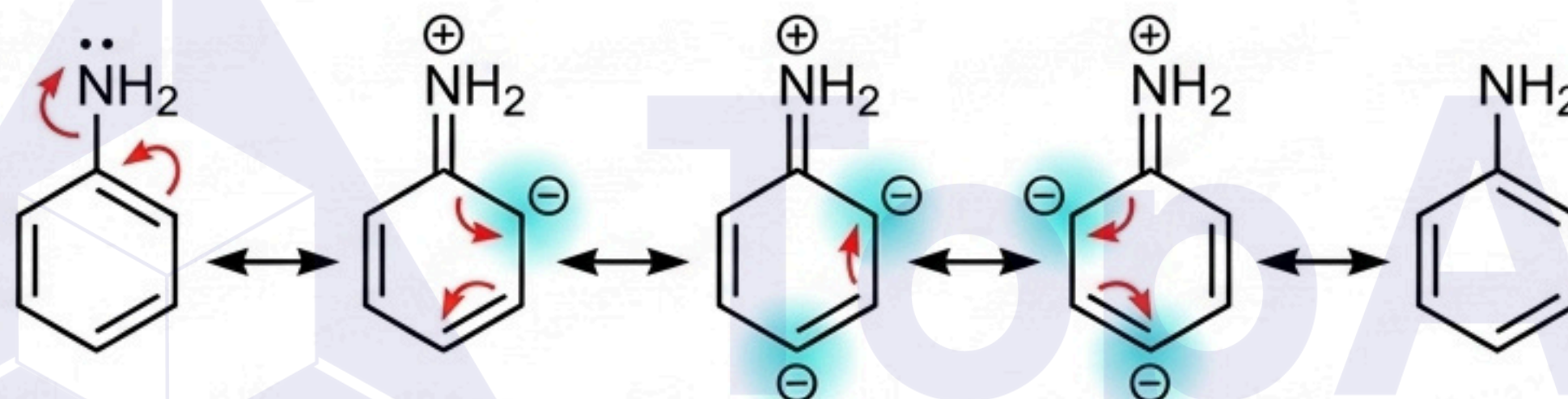


THE CORE CONCEPT

Why -NH_2 Activates the Ring

The Lone Pair

The unshared pair of electrons on the nitrogen atom is in conjugation with the benzene ring (+R effect).



Electron Density

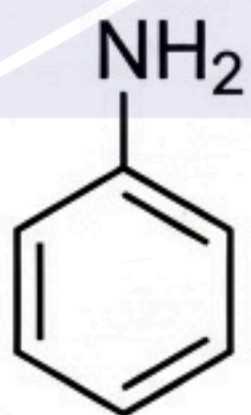
Maximum electron density localizes at the ortho- and para-positions, making them targets for electrophiles.

The -NH_2 group is an extremely powerful ortho and para directing activator.

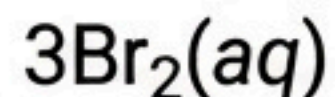
Uncontrolled Poly-Substitution: Bromination

Because the -NH_2 group is highly activating, substitution tends to occur rapidly at both ortho- and para-positions simultaneously. Monosubstitution is difficult.

Reaction Strip



+



+

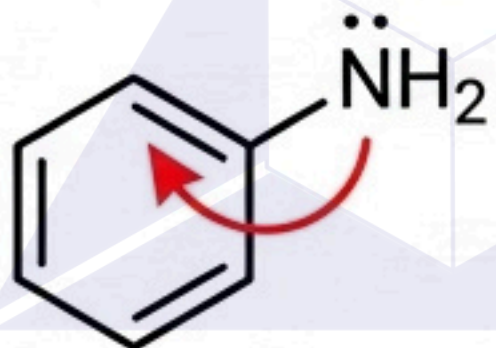


Diagnostic Observation:
White Precipitate

Protecting the Amino Group

To achieve a monosubstituted derivative, we must power down the ring's activation by protecting the -NH_2 group via acetylation.

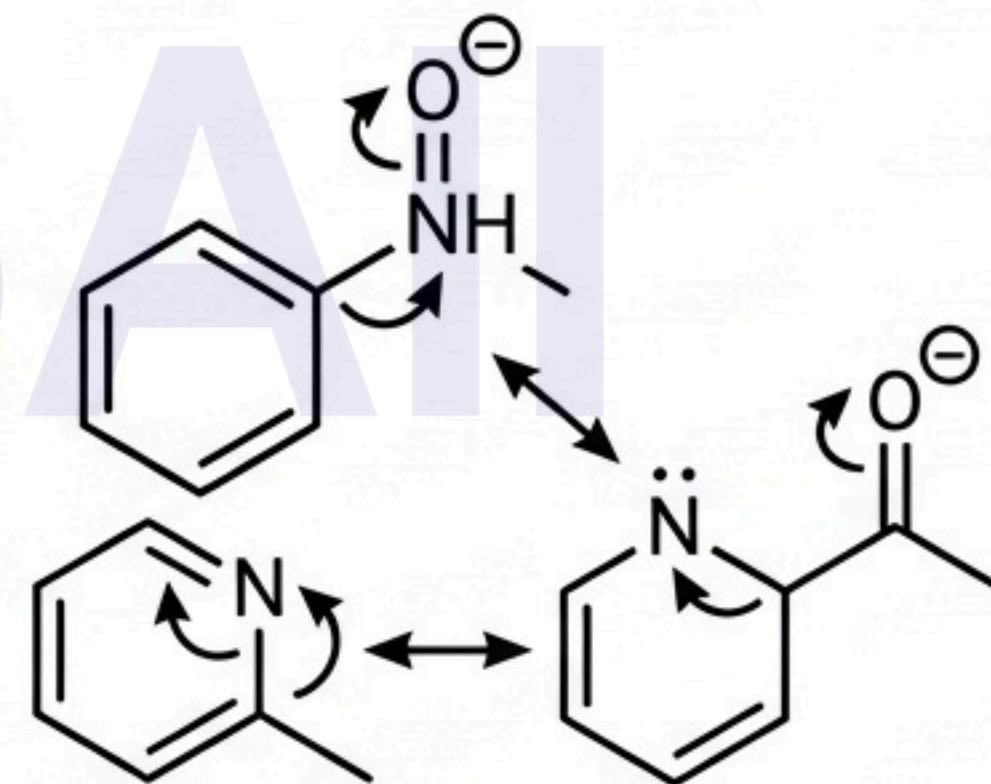
Aniline - High Activation



Formula Pill:

Reagent: Acetic Anhydride /
Pyridine

Acetanilide - Lower Activation



Key Takeaway: The activating effect of the -NHCOCH_3 group is significantly less than that of the free amino group.



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$$E=mc^2$$



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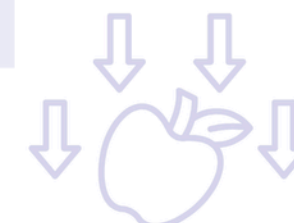
Practice Now



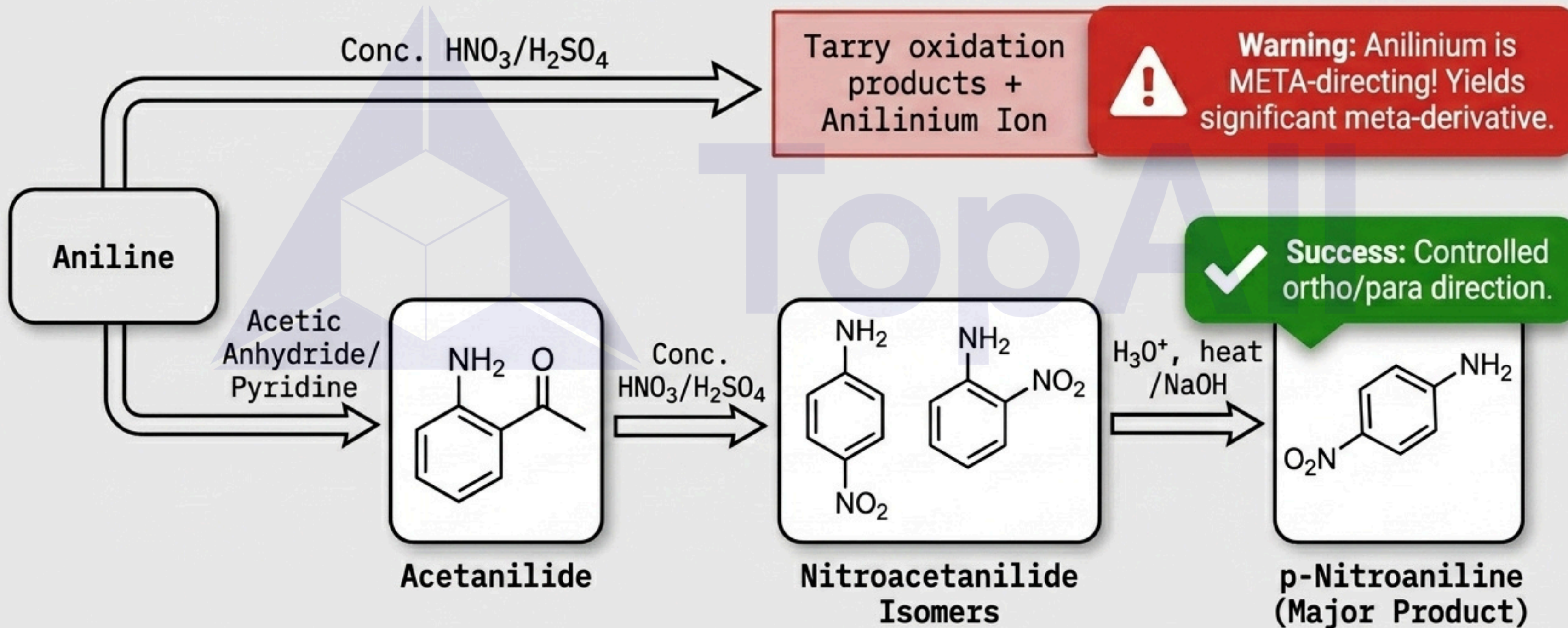
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Key Highlights

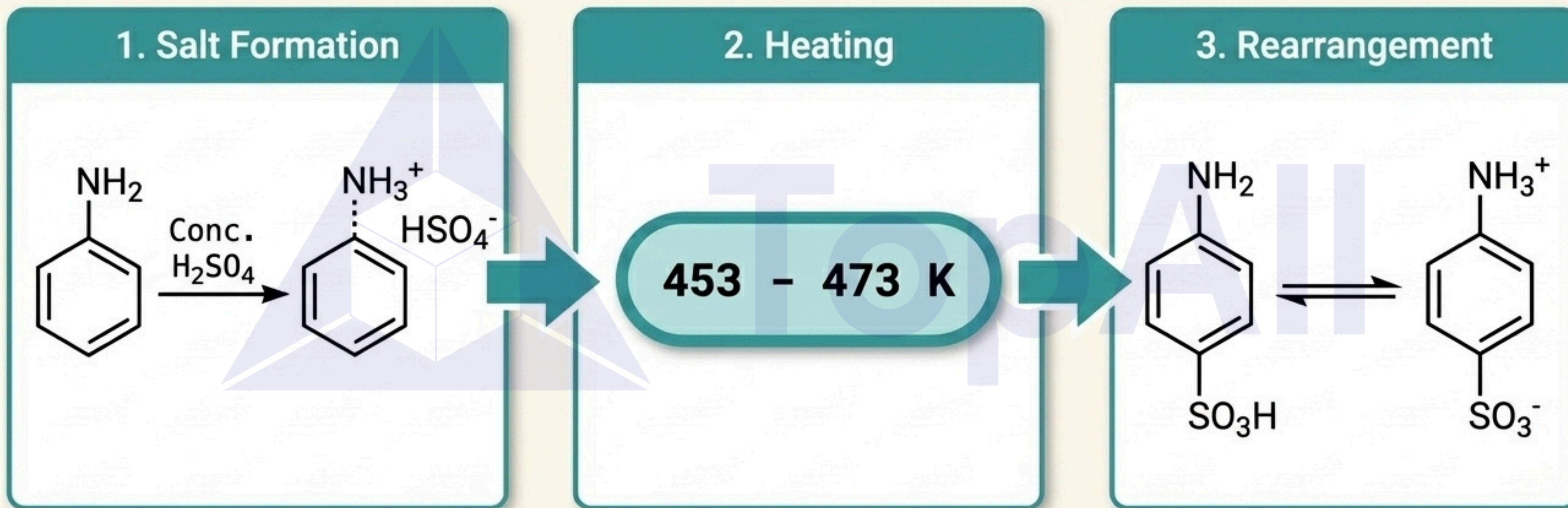
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Controlling Nitration



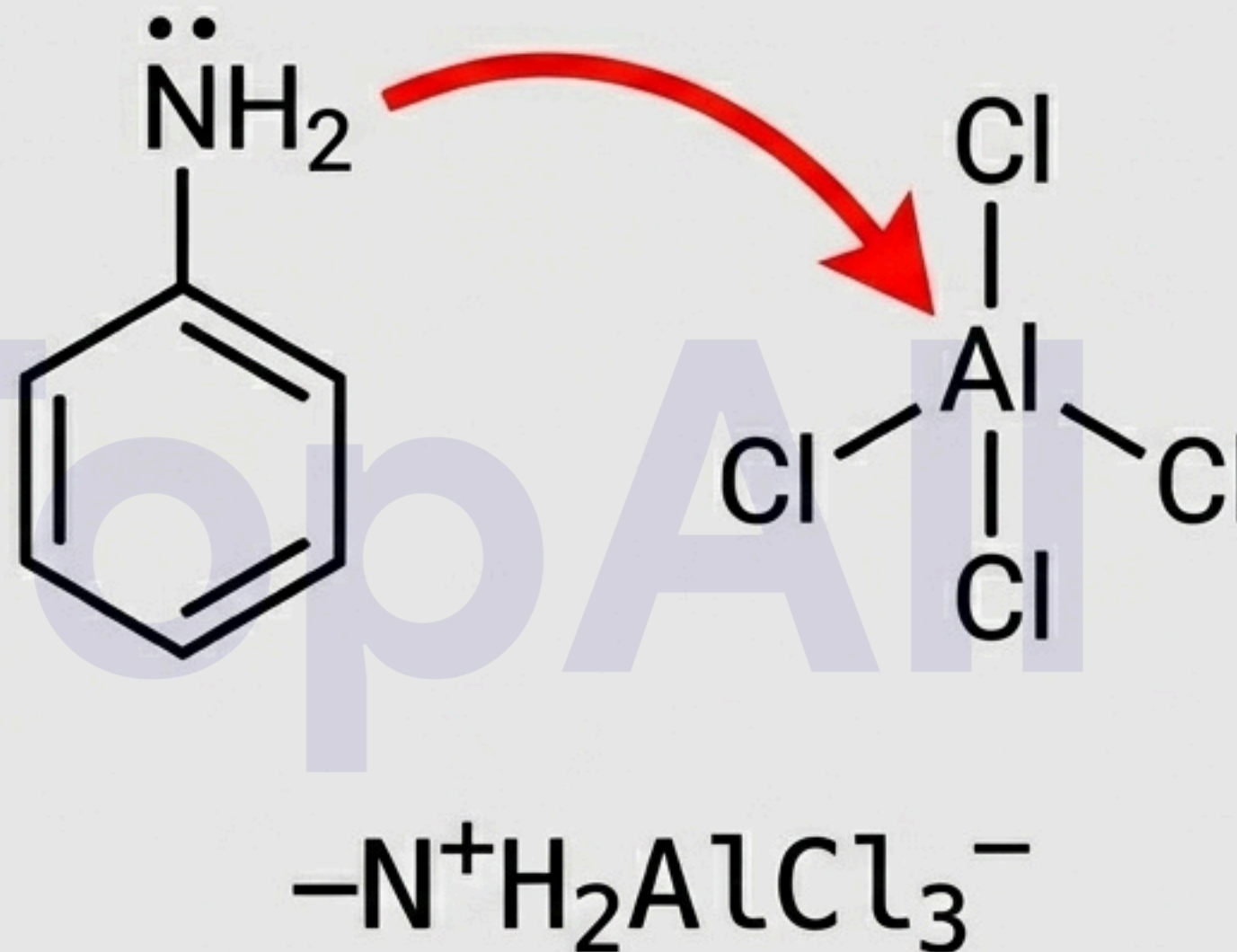
Sulphonation Pathway



Strong acidic conditions initially force salt formation, but intense heat drives the para-substitution rearrangement to form a zwitterion.

Why Friedel-Crafts Fails

Aniline does not undergo Friedel-Crafts alkylation or acylation. The basic nitrogen falls into a trap set by the Lewis acid catalyst.



Salt formation instantly converts the highly activating $-\text{NH}_2$ group into a strongly **DEACTIVATING** group, halting further electrophilic substitution.

Electrophilic Substitution Matrix

Reaction	Reagent	Direct Product Issue	Protected Product
Bromination	$\text{Br}_2(\text{aq})$	2,4,6-tribromoaniline (Over-reactivity)	p-bromoaniline (via Acetylation)
Nitration	$\text{HNO}_3/\text{H}_2\text{SO}_4$	Meta-derivative + Tarry Oxidation	p-nitroaniline (via Acetylation)
Sulphonation	Conc. H_2SO_4	Anilinium salt intermediate	Sulphanilic acid (requires 453K)
Friedel-Crafts	$\text{R-X} + \text{AlCl}_3$	FAILS (Salt complex forms)	N/A

Strategic protection of the $-\text{NH}_2$ group is the key to synthetic control in aniline chemistry.



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