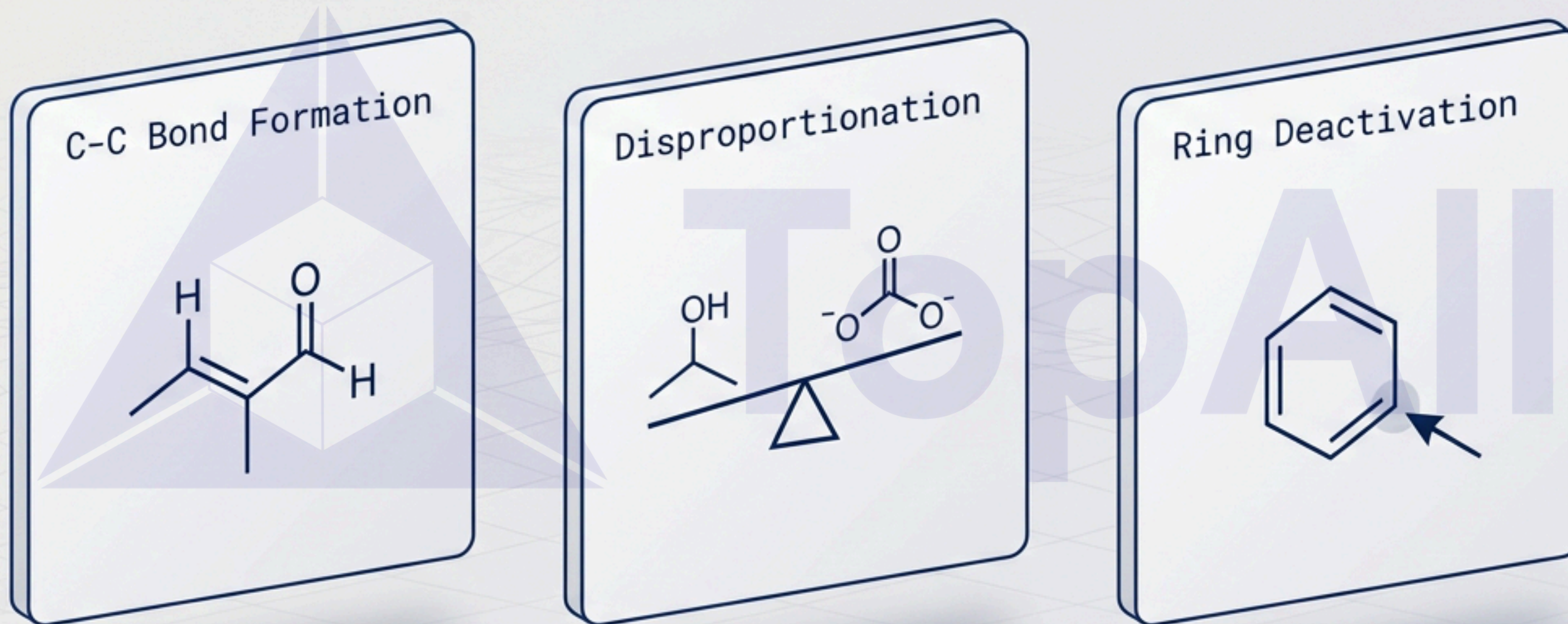


Advanced Carbonyl Reactivity

Cross Aldol, Cannizzaro and Electrophilic Substitution



[Diagnostic System Active: Structural Prerequisites]

Condition-Driven Reactivity

Cross Aldol Condensation: Expanding the Synthetic Toolkit

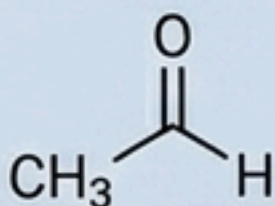
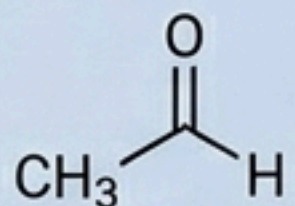
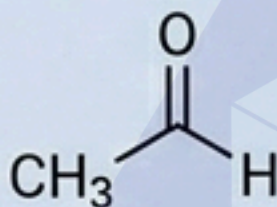
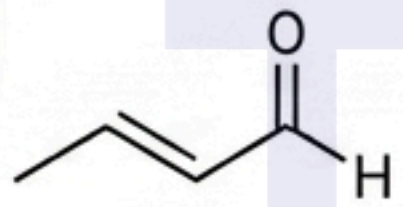
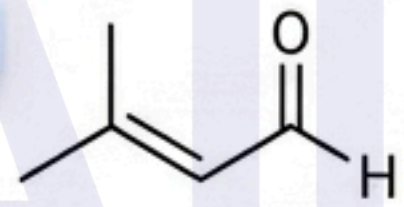
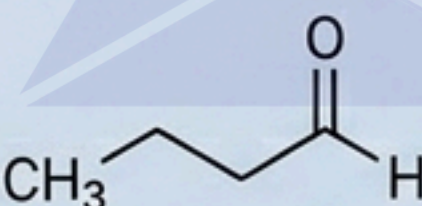
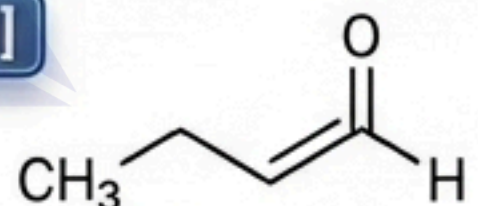
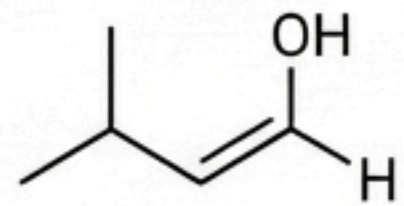


Concept Card

Mixing different aldehydes or ketones unlocks complex synthetic pathways. But if both molecules possess the necessary α -hydrogen, the reaction lacks direction, resulting in a chaotic mixture of self and cross-condensation products.

The Chaos of Mixtures

Why Mixtures Form When Both Reactants Have α -Hydrogen

		X-Axis Acts as Electrophile (Target)	
		Ethanal 	Propanal 
Y-Axis Acts as Nucleophile (Enolate)	Ethanal 	[Self Aldol]  But-2-enal	[Cross Aldol]  2-Methylbut-2-enal
	Propanal 	[Cross Aldol]  Pent-2-enal	[Self Aldol]  2-Methylpent-2-enal

Concept Card

When both molecules can act as either the attacker (nucleophile) or the target (electrophile), four distinct α,β -unsaturated products are generated.



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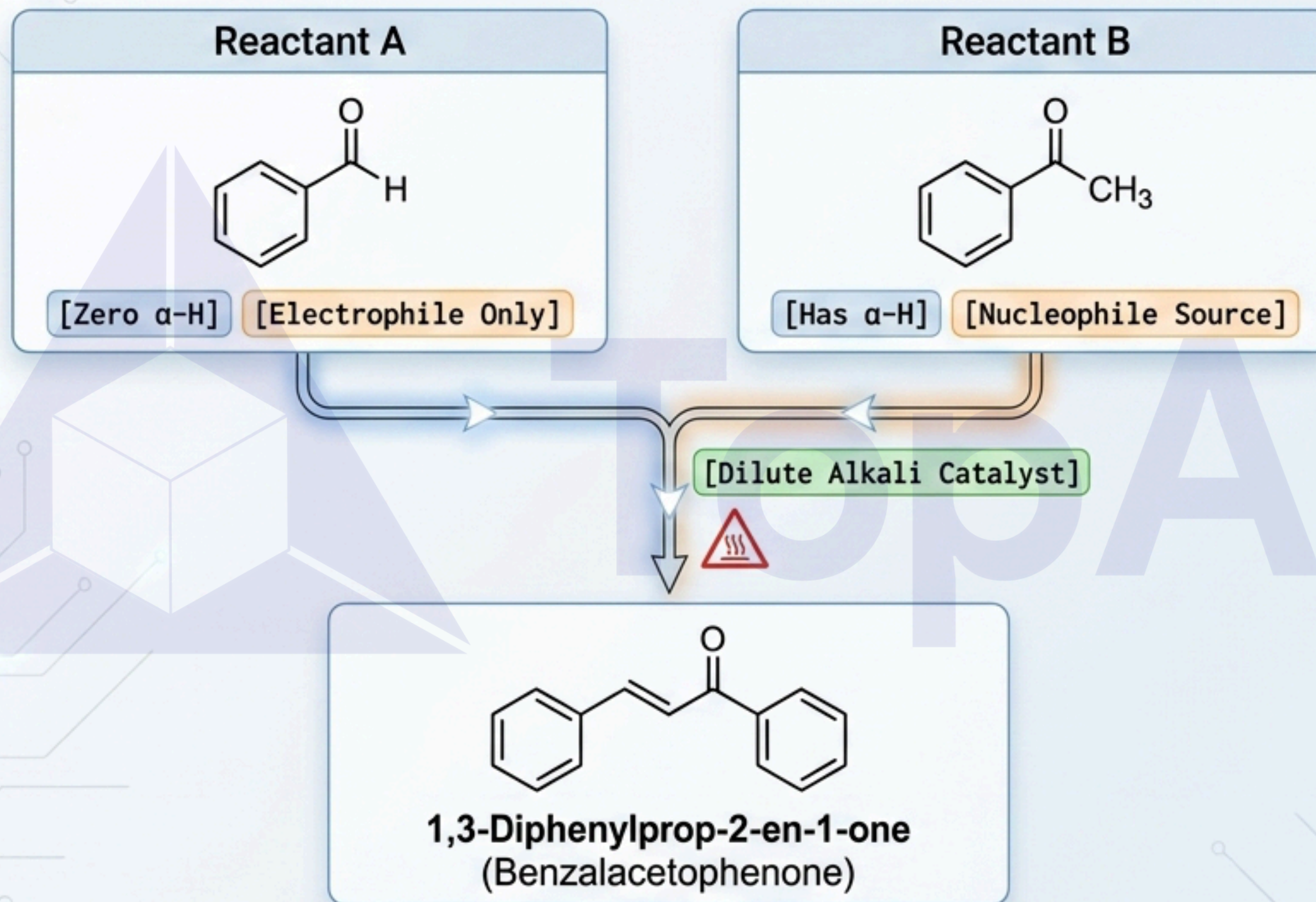
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Controlling the Reaction

Directed Cross Aldol: Forcing a Single Pathway

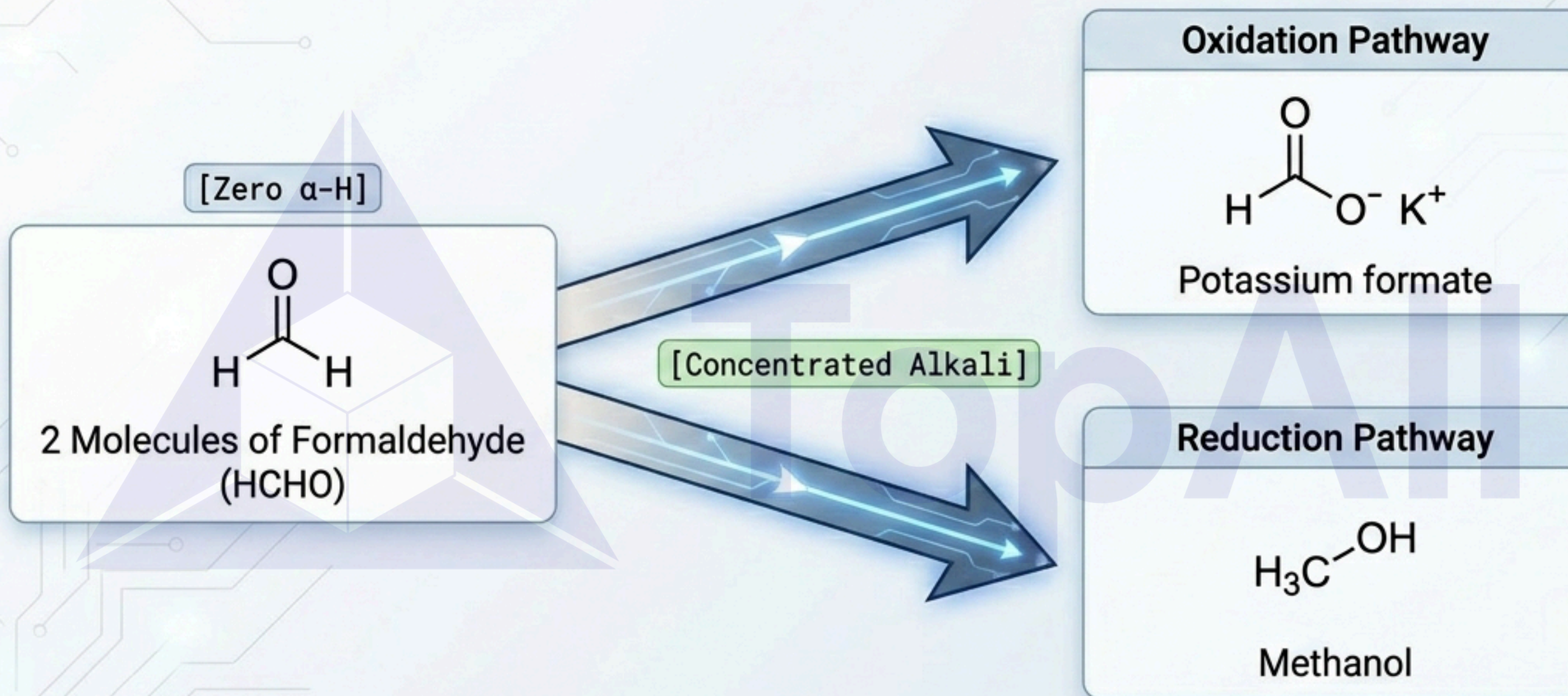


Recap Panel

By selecting one reactant completely devoid of α -hydrogens (like Benzaldehyde), we strip it of its ability to form an enolate. It is forced to be the target, yielding a single, high-yield product.

The Alternative Pathway

Cannizzaro Reaction: The Disproportionation Seesaw



Concept Card:

Aldehydes completely lacking α -hydrogens cannot undergo Aldol reactions. Instead, when heated with concentrated alkali, they react with themselves in a dramatic push-pull of electrons, simultaneously oxidizing and reducing.

Structural Destiny

Why the Pathway Diverges: The Role of the Base

Aldol Pathway

[Contains α -H]

Step 1: Base (OH^-) extracts the acidic α -proton.

Step 2: Reactive Enolate is formed.

Result: Aldol Condensation.

Role of OH^- : **Base**

Cannizzaro Pathway

[Zero α -H]

Step 1: Base (OH^-) cannot extract a proton, attacking the electrophilic carbonyl carbon directly.

Step 2: Intermediate forces a Hydride (H^-) shift to a second aldehyde molecule.

Result: Cannizzaro Disproportionation.

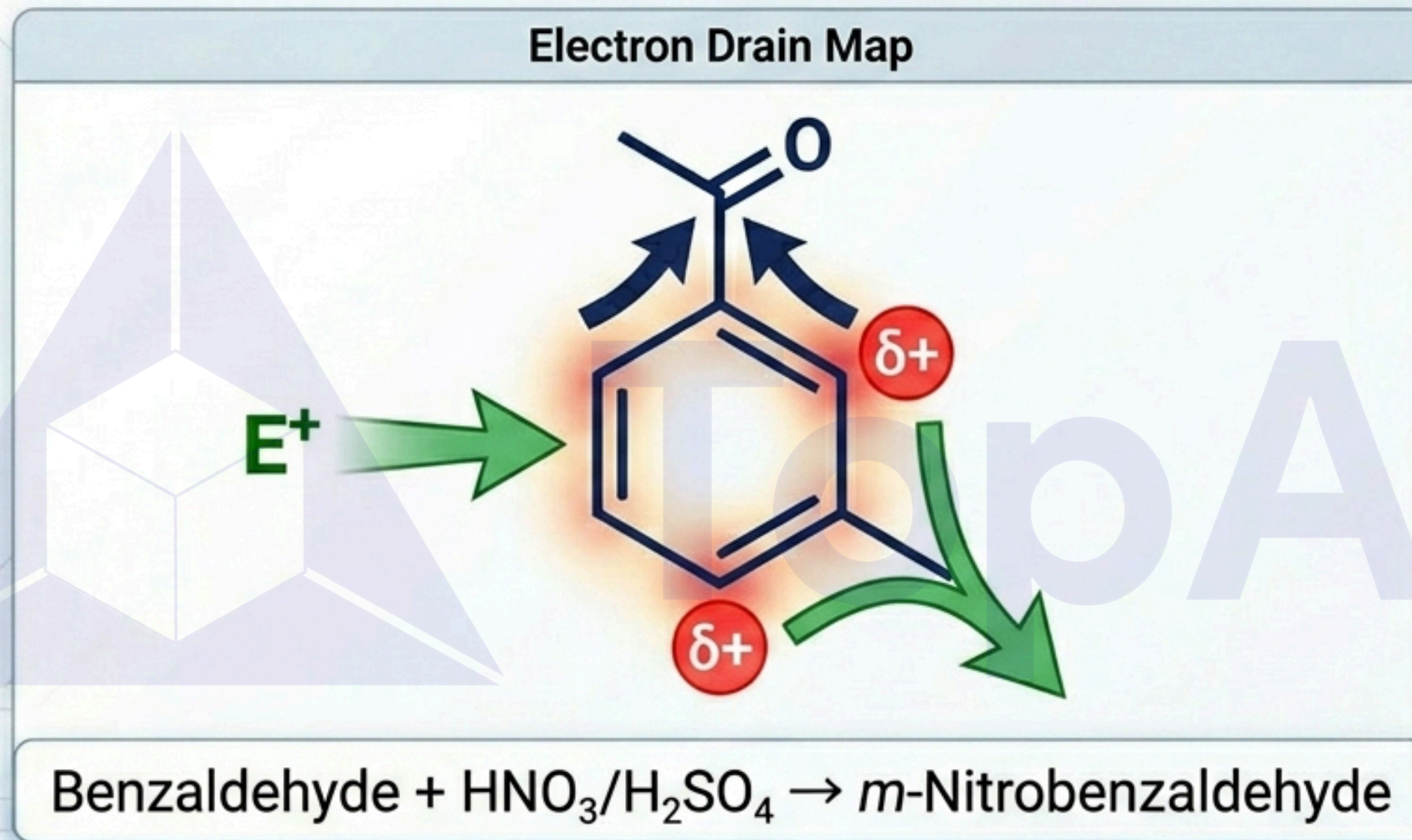
Role of OH^- : **Nucleophile**

Key-Takeaway Panel

The presence or absence of a single acidic proton fundamentally changes the role of the hydroxide ion from a base to a nucleophile.

Ring Reactivity

Electrophilic Substitution in Aromatic Aldehydes



Concept Card:

The carbonyl group acts as a powerful deactivator. By withdrawing electrons, it leaves a positive charge density at the ortho and para positions, uniquely directing any incoming electrophiles to the meta position.

Diagnostic Cheat Sheet

The Reactivity Matrix: Read the Molecule, Predict the Fate



Cross Aldol

- **Prerequisite:** [Contains α -H]
- **Reagent:** Dilute Base
- **Mechanism:** Enolate Nucleophilic Attack
- **Outcome:** C-C bond formation (α,β -unsaturated carbonyl)

Cannizzaro

- **Prerequisite:** [Zero α -H]
- **Reagent:** Conc. Base
- **Mechanism:** Hydride Shift
- **Outcome:** Disproportionation (Alcohol + Carboxylate Salt)

Aromatic EAS

- **Prerequisite:** [Aromatic Ring + Carbonyl]
- **Reagent:** Electrophile (e.g., $\text{HNO}_3/\text{H}_2\text{SO}_4$)
- **Mechanism:** Ring Deactivation
- **Outcome:** Meta-directed substitution [No Friedel-Crafts]

Anatomy dictates destiny. Diagnose the structural features, and the reaction pathway reveals itself.



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