

Aldol Condensation

Mastering the mechanism, dehydration, and the combinatorial complexity of Cross Aldol reactions.

Key Vocabulary

1. α -Hydrogen Acidity

The hydrogen atom attached to the carbon adjacent to the carbonyl group. It is uniquely acidic due to the electron-withdrawing carbonyl group and resonance stabilization.

2. Aldol / Ketol

The intermediate product containing both an aldehyde/ketone and an alcohol ($-OH$) group.

3. Cross Aldol Condensation

An aldol reaction carried out between two different aldehydes and/or ketones, resulting in a complex mixture of products.

The Mechanism Core

Two identical molecules play two different roles in dilute alkali.

Step 1: Carbanion Formation (The Nucleophile)



Step 2: Addition to Second Carbonyl (The Electrophile)



Step 3: Protonation (Forming the Aldol)



Result: 3-Hydroxybutanal (an Aldol)



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$$E=mc^2$$



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Key Highlights

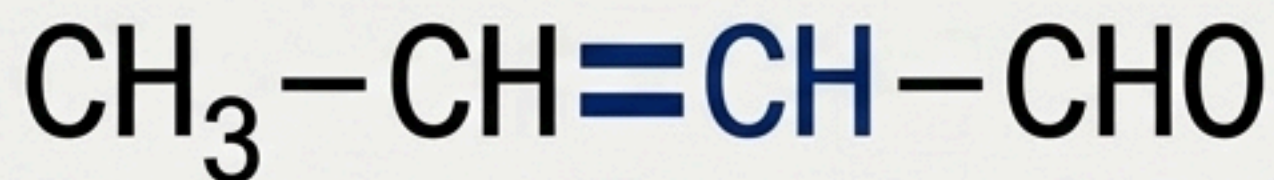
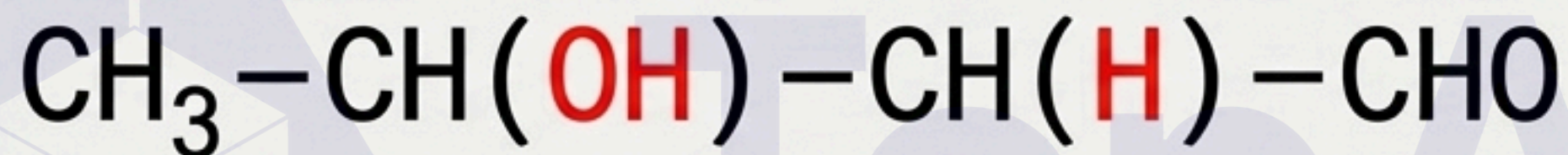
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Aldol $\rightarrow$ Condensation

The intermediate aldol readily loses water upon heating to form the final stable product.

Dehydration to α,β -Unsaturated Carbonyl



But-2-enal (Crotonaldehyde)

The Cross Aldol Matrix

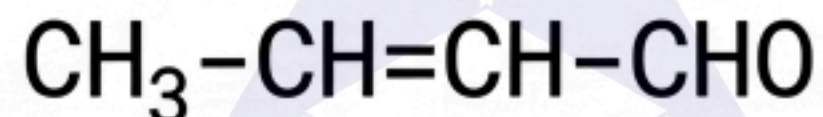
When mixing two different aldehydes (Ethanal + Propanal), we must calculate every possible Nucleophile/Electrophile combination.

	Electrophile: Ethanal	Electrophile: Propanal
Nucleophile: Ethanal	Self Aldol (Ethanal)	Cross Aldol Pathway 1
Nucleophile: Propanal	Cross Aldol Pathway 2	Self Aldol (Propanal)

The Four Products

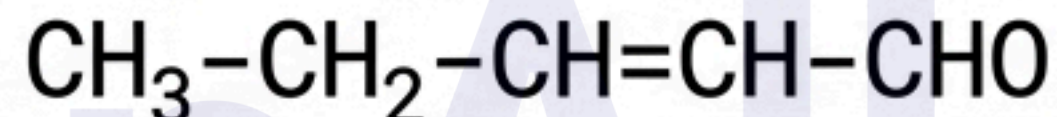
Heating the mixture from the previous slide yields these four distinct α,β -unsaturated aldehydes.

SELF (ETHANAL + ETHANAL)



But-2-enal

CROSS (NUC:ETHANAL + ELEC:PROPANAL)



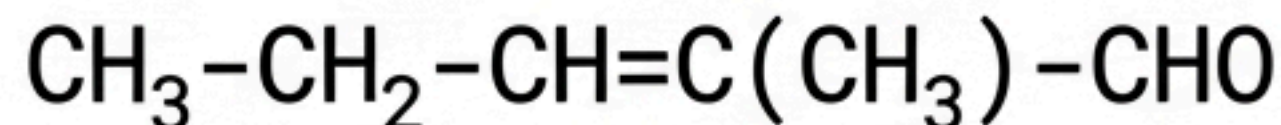
Pent-2-enal

CROSS (NUC:PROPANAL + ELEC:ETHANAL)



2-Methylbut-2-enal

SELF (PROPANAL + PROPANAL)



2-Methylpent-2-enal

Concept Check

WATCH FOR THIS

Cross aldol condensation between two different aldehydes yields a single cross product.

The Trap

Assuming only the two different molecules react with each other in one direction.

The Reality

If both partners possess α -hydrogens, expect a mixture of FOUR distinct products (2 self, 2 cross).

Final Summary

Key Takeaways

- **Mechanism Dependency:** Aldol condensation strictly requires the presence of at least one acidic α -hydrogen to form the initiating carbanion.
- **Combinatorial Outcomes:** Cross aldol condensation between two unique partners with α -hydrogens always results in a complex matrix of four structural products upon dehydration.



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