

UNIT 8 • ALDEHYDES, KETONES AND CARBOXYLIC ACIDS

# Nucleophilic Addition with Specific Reagents

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The Transformation Toolkit: Predicting  
Products and Exam Edge-Cases

## Cyanohydrin

Addition product containing both  $\text{-OH}$  and  $\text{-CN}$  groups on the same carbon; a highly useful synthetic intermediate.

## Acetal

A gem-dialkoxy compound formed by the addition of two monohydric alcohol molecules to an aldehyde.

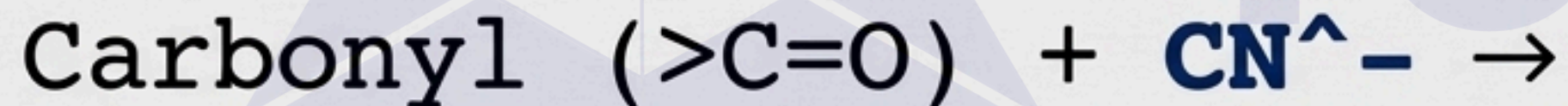
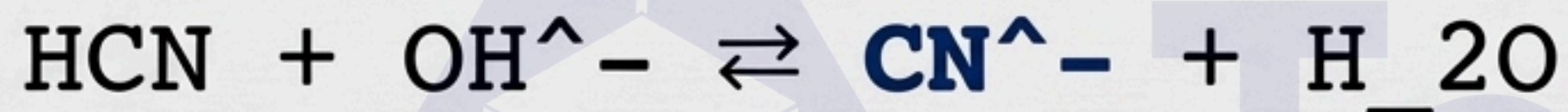
## Imine

A compound featuring a carbon-nitrogen double bond ( $\text{>C=N-}$ ), formed via rapid dehydration of an initial ammonia addition product.

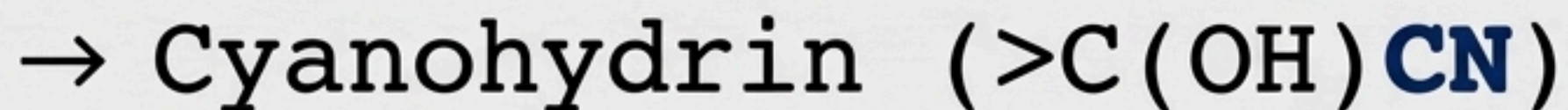
## Oxime

The specific imine derivative formed when the attacking nitrogen is attached to a hydroxyl group ( $\text{-OH}$ ).

# HCN Spotlight: Cyanohydrin Formation



Tetrahedral Intermediate  $\rightarrow$



## Why a base?

Pure HCN reacts very slowly. Base catalysis generates the much stronger  $\text{CN}^-$  nucleophile.



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

$$E=mc^2$$



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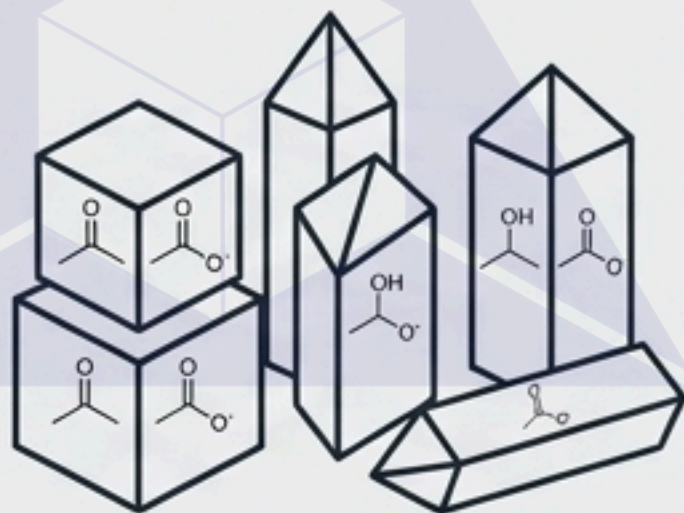
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## Key Highlights

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# NaHSO<sub>3</sub> Spotlight: Reversible Addition

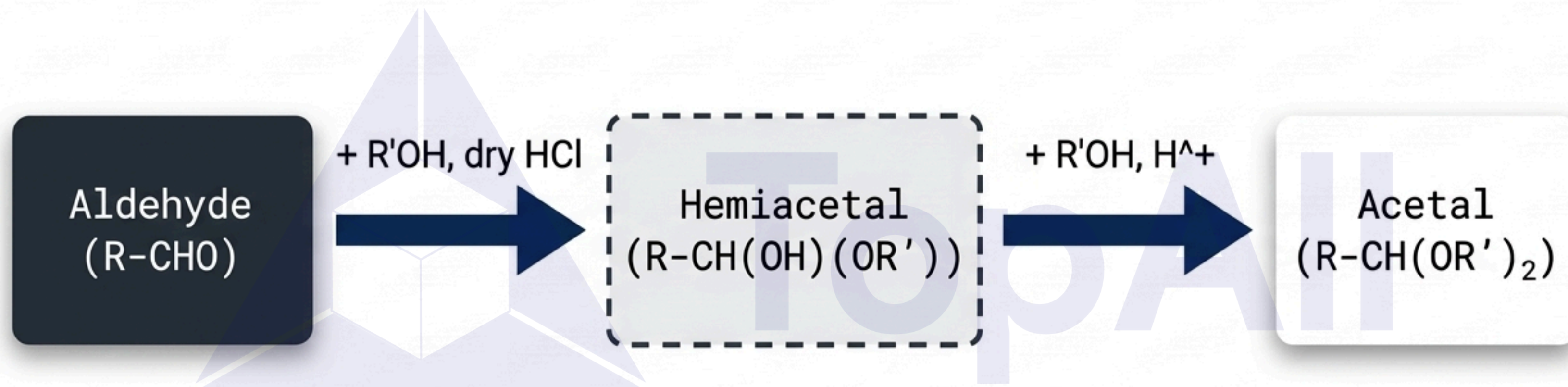


Bisulphite Addition Complex  
(Solid Crystalline Product)

## The Purification Tool

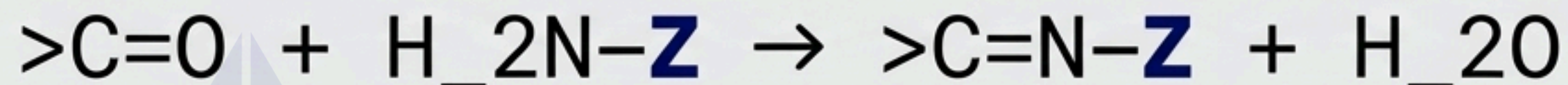
This addition product is water-soluble. Treating it with dilute mineral acid or alkali reverses the reaction, regenerating the original pure aldehyde or ketone.

# Alcohol Addition: Stepwise Transformation



For ketones → React with ethylene glycol + dry  $HCl$  to form cyclic ketals.

# The Z-Group Mapping Key



| Reagent Structure               | Reagent Name  | Product Name         |
|---------------------------------|---------------|----------------------|
| $\mathbf{Z} = -\text{OH}$       | Hydroxylamine | <b>Oxime</b>         |
| $\mathbf{Z} = -\text{NH}_2$     | Hydrazine     | <b>Hydrazone</b>     |
| $\mathbf{Z} = -\text{NHCONH}_2$ | Semicarbazide | <b>Semicarbazone</b> |

The reaction is reversible and acid-catalyzed. Equilibrium favors the product due to rapid dehydration.

# Characterisation Card: The 2,4-DNP Test



**Reagent :** 2,4-Dinitrophenylhydrazine  
(where Z =  $-\text{NH}-\text{C}_6\text{H}_3(\text{NO}_2)_2$ ).

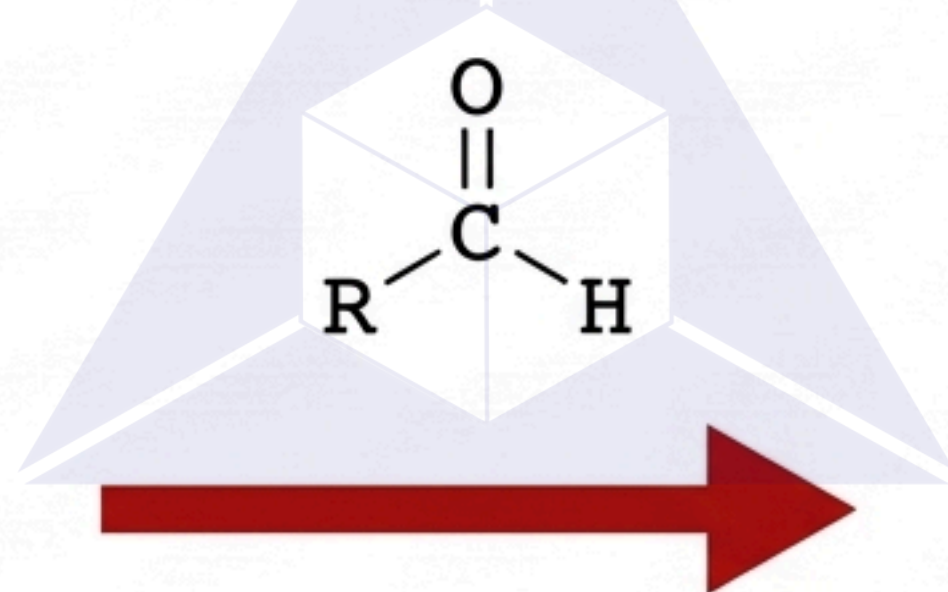
**The Result :** Produces 2,4-DNP derivatives which are distinctly yellow, orange, or red solids.

**Lab Utility :** Used as a definitive visual characterization test to confirm the presence of an aldehyde or ketone.

# JEE Trap Alert: The Steric Shift

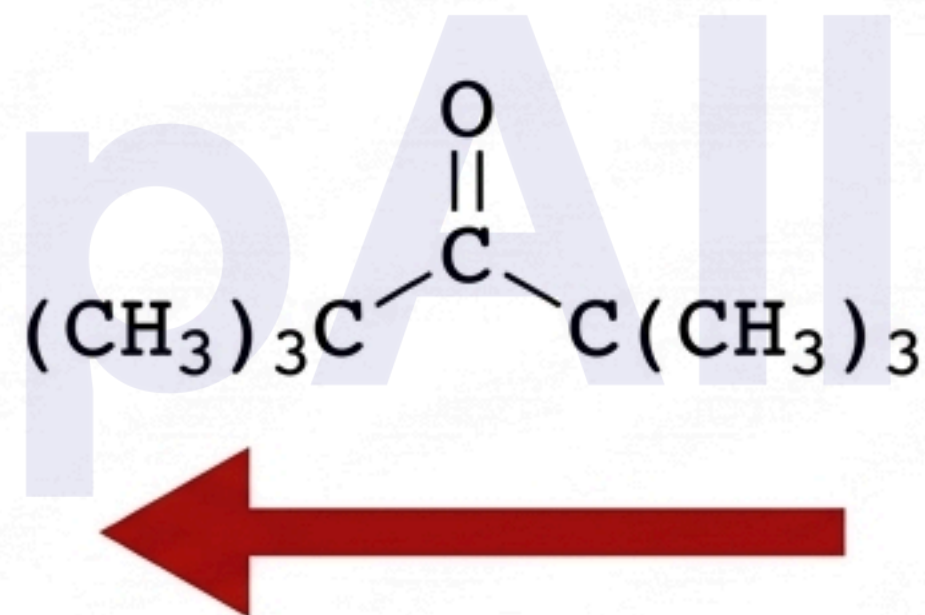
Watch for this steric shift in  $\text{NaHSO}_3$  addition...

## Aldehydes



Addition is highly favored.

## Ketones



Two large alkyl substituents create steric hindrance, blocking the nucleophile and shifting equilibrium away from the product.

# Synthesis Complete: Key Takeaways

Nucleophilic addition relies on pattern recognition: always track the attacking nucleophile (e.g., base-generated  $\text{CN}^-$ , or the  $\text{H}_2\text{N}-\text{Z}$  group).

Always account for steric and electronic factors: large substituents on ketones not only reduce electrophilicity but can completely shift equilibrium (e.g.,  $\text{NaHSO}_3$  blocking).



# You've Learned the Theory.

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