

Oxidation Reactions of Aldehydes and Ketones

Mastering diagnostic tests, structural cleavage,
and high-yield exam traps.

DIAGNOSTIC TOOLKIT INTRODUCTION

Tollens' Test

The universal aldehyde detector.

Uses ammoniacal silver nitrate to identify the presence of any aldehyde group.

Fehling's Test

The aliphatic aldehyde detector.

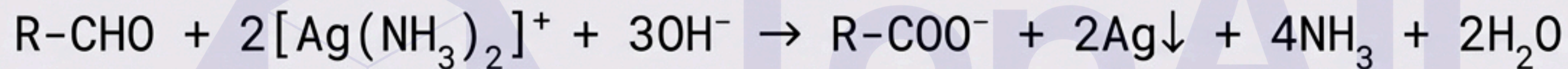
Uses aqueous copper sulphate + Rochelle salt. (A more selective tool).

Haloform Reaction

The methyl ketone detector.

Uses sodium hypohalite to identify carbonyls linked directly to a -CH₃ group.

Tollens' Test: The Silver Mirror



Formation of a bright silver metal mirror. The aldehyde is oxidized to a carboxylate anion in an alkaline medium.



**You've Learned the Theory.
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$$E=mc^2$$



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Key Highlights

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Fehling's Test: The Reddish-Brown Precipitate

The Reagents



Fehling A (CuSO_4)

Fehling B
(alkaline sodium
potassium tartrate /
Rochelle salt)

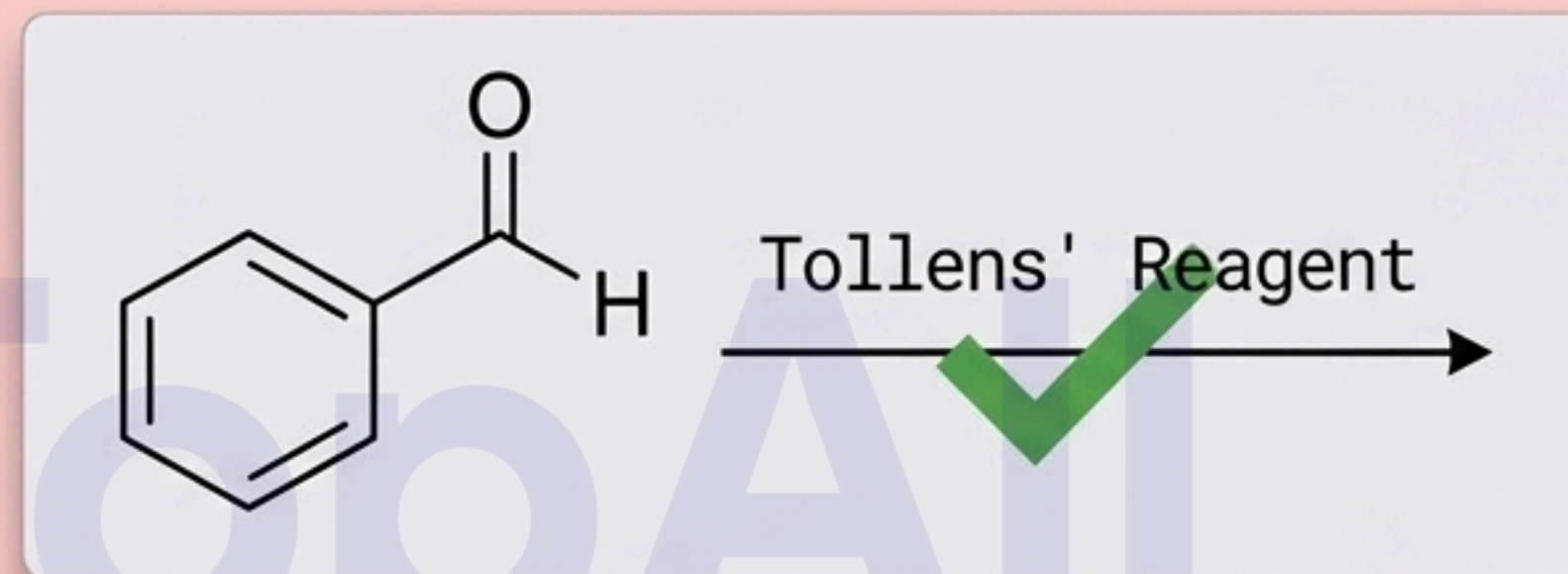
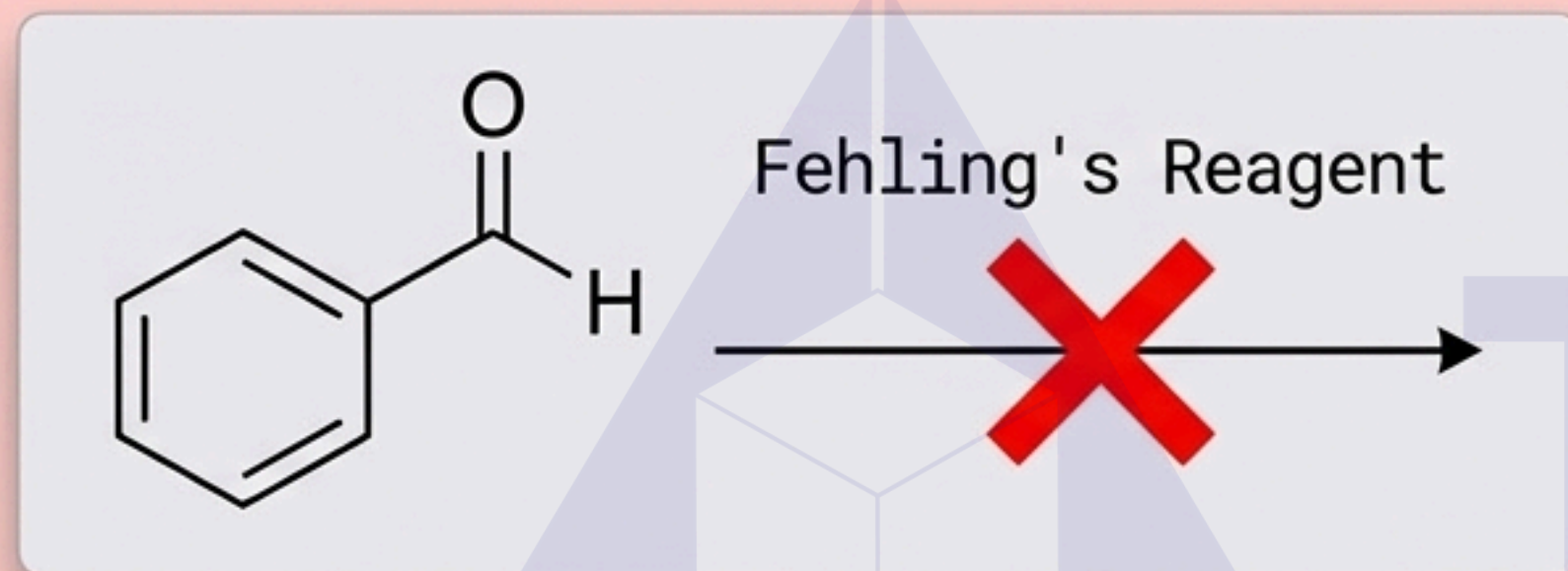
The Result



Reddish-brown
precipitate.

Works on Aliphatic Aldehydes ONLY.

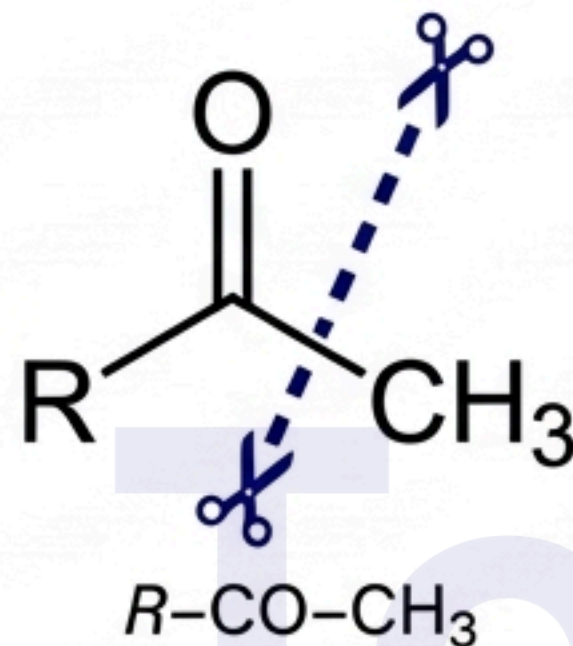
Watch for this: Differentiating Aliphatic vs. Aromatic Aldehydes



Benzaldehyde fails Fehling's test. The carbonyl carbon is less electrophilic due to resonance with the aromatic ring, making it resistant to Fehling's milder oxidation.

**Always use Tollens' test to detect aromatic aldehydes;
Fehling's will yield a false negative.**

Haloform Reaction: Targeted Cleavage



Target: Methyl Ketones (must have at least one $-CH_3$ linked to carbonyl).

Reagent: Sodium hypohalite ($NaOX$).

Products (Post-Cleavage): Yields a Haloform (CHX_3) + Sodium salt of a carboxylic acid.

The resulting carboxylate has ONE CARBON ATOM LESS than the parent ketone.
 $C=C$ double bonds remain unaffected.

Ketone C-C Cleavage: The Brute Force Approach

Mild Conditions



Tollens' / Fehling's $\rightarrow$ No Reaction

Ketones robustly resist mild oxidizers.

Vigorous Conditions



Strong agents (HNO_3 , KMnO_4 , $\text{K}_2\text{Cr}_2\text{O}_7$) + Elevated Heat

Forced carbon-carbon bond cleavage. Splits a single ketone into a MIXTURE of carboxylic acids, each containing fewer carbon atoms than the parent molecule.

Key Takeaways

- Aldehydes oxidize easily and are distinguished by Tollens' (universal detection) and Fehling's (aliphatic only) tests.
- Ketones resist mild oxidation, requiring vigorous C-C cleavage, except for methyl ketones which undergo targeted cleavage via the haloform reaction.



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