

Chapter 8 · Aldehydes, Ketones and Carboxylic Acids

CBSE Class 12 Chemistry (043) · Organic · Unit 8 = 8 marks (highest in organic) · Ultimate Revision Sheet

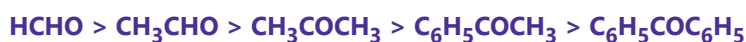
60-SECOND RECALL

Reactivity to Nu	$\text{HCHO} > \text{CH}_3\text{CHO} > \text{ketone}$ — steric + electronic
Tollens	Silver mirror — aldehyde only
Fehling	Red-brown Cu_2O — aliphatic aldehyde only (not aromatic)
Iodoform	Needs $\text{CH}_3\text{CO}-$ or $\text{CH}_3\text{CH}(\text{OH})-$ → yellow CHI_3
Aldol	Needs α -hydrogen
Cannizzaro	Needs NO α -hydrogen (HCHO , $\text{C}_6\text{H}_5\text{CHO}$)
Acidity	Carboxylic acid > phenol > alcohol
HVZ	$\text{X}_2/\text{red P} \rightarrow \alpha$ -halo acid (needs α -H)

1. The Carbonyl Group

STRUCTURE AND REACTIVITY The carbonyl carbon is sp^2 , planar, and carries δ^+ — so it is attacked by nucleophiles (unlike alkenes, which attract electrophiles).

Order of reactivity towards nucleophilic addition:



Two reasons, always give both: (1) +I effect of alkyl groups reduces the δ^+ on carbon; (2) steric hindrance blocks the nucleophile. Aryl groups also deactivate by resonance.

2. Preparation

THE ROUTES ASKED Aldehydes: oxidation of 1° alcohol with PCC; Rosenmund reduction (acid chloride + $\text{H}_2/\text{Pd}-\text{BaSO}_4$); Stephen reaction (nitrile + SnCl_2/HCl); DIBAL-H on nitriles or esters.

Ketones: oxidation of 2° alcohol; acid chloride + dialkylcadmium; Friedel-Crafts acylation for aryl ketones.

From alkynes: hydration of ethyne gives acetaldehyde; any other alkyne gives a ketone.

Carboxylic acids: oxidation of 1° alcohol or aldehyde; hydrolysis of nitriles; Grignard + CO_2 then H^+ (adds one carbon).

3. Reactions of Aldehydes and Ketones

NUCLEOPHILIC ADDITION $\text{HCN} \rightarrow$ cyanohydrin · $\text{NaHSO}_3 \rightarrow$ bisulphite adduct (used to purify carbonyls) · alcohol $\rightarrow$ hemiacetal then acetal · Grignard $\rightarrow$ alcohol.

Addition-elimination with ammonia derivatives: with 2,4-DNP $\rightarrow$ orange-yellow precipitate (the standard test for a carbonyl group); with $\text{NH}_2\text{OH} \rightarrow$ oxime; with $\text{NH}_2\text{NH}_2 \rightarrow$ hydrazone.

THE TWO REACTIONS DECIDED BY α -HYDROGEN Aldol condensation — requires at least one α -H. Two molecules combine in dilute alkali to give a β -hydroxy aldehyde or ketone, which on heating loses water to give an α,β -unsaturated product.

Cannizzaro reaction — requires **NO** α -H. With concentrated alkali the aldehyde disproportionates into an alcohol and a salt of the acid. Classic examples: HCHO and benzaldehyde.

Check the α -hydrogen first and the question answers itself.

OXIDATION AND REDUCTION Aldehydes oxidise easily to acids; ketones resist oxidation and need drastic conditions (C-C cleavage, Popoff's rule).

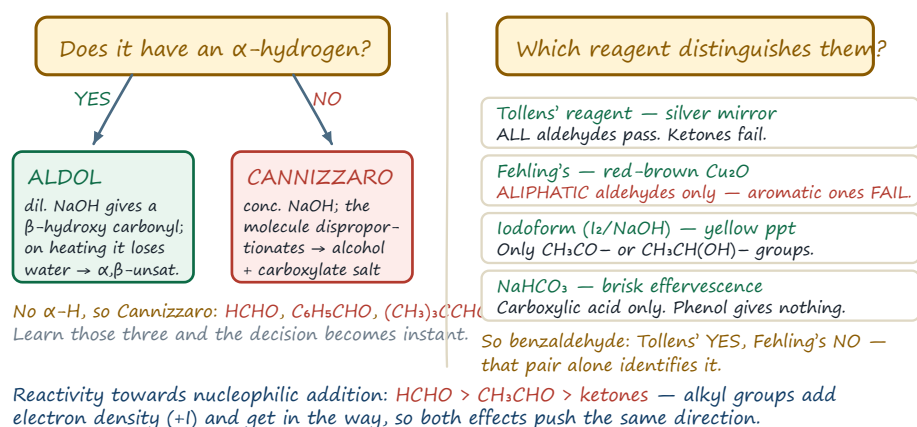
Reduction: NaBH4/LiAlH4 → alcohol. To go all the way to the hydrocarbon: **Clemmensen** (Zn-Hg/HCl, acidic) or **Wolff-Kishner** (NH2NH2/KOH, basic). Pick by whether the molecule tolerates acid or base.

THE DISTINGUISHING TESTS — know exactly what each detects

Test	Positive result	Detects
Tollens' (ammoniacal <chem>AgNO3</chem>)	Silver mirror	All aldehydes ; ketones do not respond
Fehling's	Red-brown ppt of <chem>Cu2O</chem>	Aliphatic aldehydes only — aromatic ones fail
Iodoform (<chem>I2/NaOH</chem>)	Yellow <chem>CHI3</chem>	<chem>CH3CO-</chem> or <chem>CH3CH(OH)-</chem> group
2,4-DNP	Orange-yellow ppt	Any aldehyde or ketone

The classic exam pair: benzaldehyde gives Tollens' but **not** Fehling's. Acetone gives iodoform but **not** Tollens'.

Two decisions settle almost every carbonyl question



If a question gives you conc. NaOH and an aldehyde with no α -H, it is Cannizzaro every time. If it gives dil. NaOH and an α -H is present, it is aldol.

4. Carboxylic Acids

ACIDITY — the reasoning asked The carboxylate ion is resonance stabilised over two equivalent oxygens, which makes the acid far stronger than phenol (where the charge is spread over carbon atoms) or an alcohol.

Electron-withdrawing groups increase acidity: $\text{FCH}_2\text{COOH} > \text{ClCH}_2\text{COOH} > \text{BrCH}_2\text{COOH}$, and $\text{Cl}_3\text{CCOOH} > \text{Cl}_2\text{CHCOOH} > \text{ClCH}_2\text{COOH}$.

The effect falls off with distance: 2-chlorobutanoic acid is stronger than 3-chloro, which is stronger than 4-chloro.

Electron-donating groups decrease acidity: $\text{HCOOH} > \text{CH}_3\text{COOH} > \text{CH}_3\text{CH}_2\text{COOH}$.

REACTIONS With $\text{NaHCO}_3 \rightarrow$ brisk effervescence of CO_2 — this distinguishes a carboxylic acid from a phenol, which does not react.

Esterification with alcohol/ H^+ · $\text{SOCl}_2 \rightarrow$ acid chloride · NH_3 then heat $\rightarrow$ amide · $\text{LiAlH}_4 \rightarrow$ 1° alcohol (NaBH_4 will not reduce an acid).

Decarboxylation: sodium salt + soda lime $\rightarrow$ alkane with one carbon less.

HVZ reaction: $\text{X}_2/\text{red P}$ gives the α -halo acid — requires an α -hydrogen, so HCOOH does not undergo it.

WORKED EXAMPLE — a typical identification question An organic compound gives a silver mirror with Tollens', no colour with Fehling's, and undergoes Cannizzaro with conc. NaOH . Identify it.

Tollens' positive $\rightarrow$ it is an aldehyde

Fehling's negative $\rightarrow$ it is aromatic

Cannizzaro $\rightarrow$ it has no α -hydrogen

$\Rightarrow$ the compound is benzaldehyde, $\text{C}_6\text{H}_5\text{CHO}$.

5. Question Triggers what the reagent tells you

Reagent / observation	Conclusion
Tollens' positive, Fehling's negative	Aromatic aldehyde
Iodoform positive	Has $\text{CH}_3\text{CO}-$ or $\text{CH}_3\text{CH}(\text{OH})-$
Effervescence with NaHCO_3	Carboxylic acid (phenol gives none)
Conc. NaOH , no α -H	Cannizzaro
Dilute NaOH , has α -H	Aldol
$\text{Zn-Hg} / \text{HCl}$	Clemmensen $\rightarrow \text{C=O to CH}_2$
$\text{NH}_2\text{NH}_2 / \text{KOH}$, glycol	Wolff-Kishner $\rightarrow \text{C=O to CH}_2$
$\text{H}_2/\text{Pd-BaSO}_4$	Rosenmund $\rightarrow$ aldehyde
$\text{X}_2 / \text{red P}$	HVZ $\rightarrow \alpha$ -halo acid

MOST-ASKED BOARD QUESTIONS

- [3M] Distinguish between the given pairs of compounds using chemical tests.
- [3M] Explain the aldol and Cannizzaro reactions with mechanisms and examples.
- [3M] Arrange given acids in order of acidity and justify.

4. [2M] Why are aldehydes **more reactive than ketones** towards nucleophilic addition?
5. [2M] Conversion chains, e.g. ethanol $\rightarrow$ ethanoic acid $\rightarrow$ ethanoyl chloride $\rightarrow$ ethanamide.
6. [1M] Which reagent distinguishes a carboxylic acid from a phenol? $\rightarrow$ **NaHCO_3**

THE HABIT THAT SCORES — For any aldehyde/ketone question, ask two things in order: **does it have an α -hydrogen?** and **is it aromatic?** Those two answers decide aldol vs Cannizzaro and Fehling's vs Tollens' — which between them account for most of the marks in this unit.