▶ Video explanation (YouTube Short)

Aldehydes, Ketones and Carboxylic Acids: Chapter Recap

The whole chapter is the story of one group, the **carbonyl group C=O**, and of the carboxyl group –COOH built on it.

1. The carbonyl group

The carbonyl carbon is sp² hybridised and the group is planar (bond angles about 120°). The C=O bond is polar: oxygen is δ^-, carbon is δ^+. The δ^+ carbon is attacked by nucleophiles.

2. Preparation of aldehydes and ketones

From	Reagent	Gives
1° / 2° alcohol	oxidation (e.g. PCC for aldehydes; $K_2Cr_2O_7/H^+$ for ketones)	aldehyde / ketone
alkene	O_3, then Zn/H_2O (ozonolysis)	aldehydes and/or ketones
alkyne	H_2O, dil. H_2SO_4, $HgSO_4$	ethanal (from ethyne) or ketones
acyl chloride	H_2, Pd–$BaSO_4$ (Rosenmund reduction)	aldehyde
other routes	Stephen reduction, Etard reaction, Gatterman-Koch, Friedel-Crafts acylation	aldehydes / aromatic ketones

3. Nucleophilic addition

The nucleophile attacks the δ^+ carbonyl carbon; the C=O π electrons move onto oxygen, giving a tetrahedral intermediate that takes up a proton.

Reagent	Product
HCN	cyanohydrin
alcohol (dry HCl)	hemiacetal, acetal (ketal from ketones)
NH_2–Z (NH_2OH, NH_2NH_2, …)	oxime, hydrazone, … (addition then loss of water)

4. α-Hydrogen, tests

- With an α-hydrogen, dilute alkali: **aldol** reaction / condensation.
- Without an α-hydrogen (HCHO, C_6H_5CHO), concentrated alkali: **Cannizzaro** reaction (one molecule oxidised, one reduced).
- **Tollens' reagent**: aldehydes give a silver mirror.
- **Fehling's solution**: aliphatic aldehydes give a red-brown precipitate (Cu_2O).
- Ketones generally give neither test.

5. Carboxylic acids

The carboxylate ion $RCOO^-$ is stabilised by resonance: the negative charge is shared equally by both oxygens (two equal C–O bonds). This makes carboxylic acids acidic (more than alcohols and phenols). Electron-withdrawing groups increase acidity; electron-donating groups decrease it. –COOH forms esters, acid chlorides, anhydrides and amides; HVZ gives α-halo acids; –COOH on a ring is meta-directing.

Solved example

Q. Which of ethanal and benzaldehyde gives the aldol reaction, and which gives the Cannizzaro reaction?
A. Ethanal (CH_3CHO) has α-hydrogens, so it gives the aldol reaction with dilute alkali. Benzaldehyde has no α-hydrogen, so with concentrated alkali it gives the Cannizzaro reaction.

Key takeaways

- Polar C=O: δ^- O, δ^+ C.
- The typical reaction is nucleophilic addition.
- α-H: aldol; no α-H: Cannizzaro.
- Tollens' and Fehling's distinguish aldehydes from ketones.
- Carboxylate resonance makes carboxylic acids acidic.

Practice questions

1. (MCQ) The hybridisation of the carbonyl carbon is: (a) sp (b) sp^2 (c) sp^3 (d) dsp^2
2. (MCQ) Which gives the Cannizzaro reaction? (a) CH_3CHO (b) CH_3COCH_3 (c) C_6H_5CHO (d) CH_3CH_2CHO
3. (MCQ) Rosenmund reduction converts an acyl chloride into: (a) an alcohol (b) an aldehyde (c) a ketone (d) an acid
4. (Very short) Name the product of the addition of HCN to a ketone.
5. (Very short) Which reagent gives a silver mirror with aldehydes?
6. (Short) Why are aldehydes and ketones attacked by nucleophiles at the carbonyl carbon?
7. (Short) Why is a carboxylic acid more acidic than an alcohol?
8. (Application) Give a chemical test to distinguish propanal from propanone.

Answer key

1. (b) sp^2.
2. (c) C_6H_5CHO (no α-hydrogen).
3. (b) an aldehyde.
4. A cyanohydrin.
5. Tollens' reagent (ammoniacal silver nitrate).
6. The C=O bond is polar: oxygen pulls the electrons, leaving the carbon δ^+ (electron-poor), so the electron-rich nucleophile attacks it.
7. The carboxylate ion is stabilised by resonance (charge shared by two oxygens); the alkoxide ion has no such resonance.
8. Propanal gives a silver mirror with Tollens' reagent (and a red-brown precipitate with Fehling's solution); propanone gives neither.

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