

Carbonyl compounds

A-Level Chemistry 9701 · Topic 17 revision notes

Everything from the 2 lessons of this topic on a few pages: the key idea of each lesson, the diagram to remember, the points to learn and the traps examiners set. Read it, cover it, test yourself.

1. Aldehydes and ketones

2. Nucleophilic addition and carbonyl tests

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1 Aldehydes and ketones

Syllabus 17.1

Aldehydes and ketones are **carbonyl compounds**: both contain $C=O$. In an **aldehyde** ($RCHO$, names ending in -al) the $C=O$ is at the end of the chain with an H attached; in a **ketone** ($RCOR'$, names ending in -one) it is bonded to two carbons. A **primary alcohol** is oxidised by acidified $K_2Cr_2O_7$ to an aldehyde, which must be **distilled off** as it forms or it is oxidised further to a carboxylic acid (as happens under **reflux**). A **secondary alcohol** gives a ketone, which resists further oxidation. **$NaBH_4$** (or $LiAlH_4$) reduces aldehydes back to primary alcohols and ketones back to secondary alcohols.

oxidation [O] to the right, reduction [H] to the left

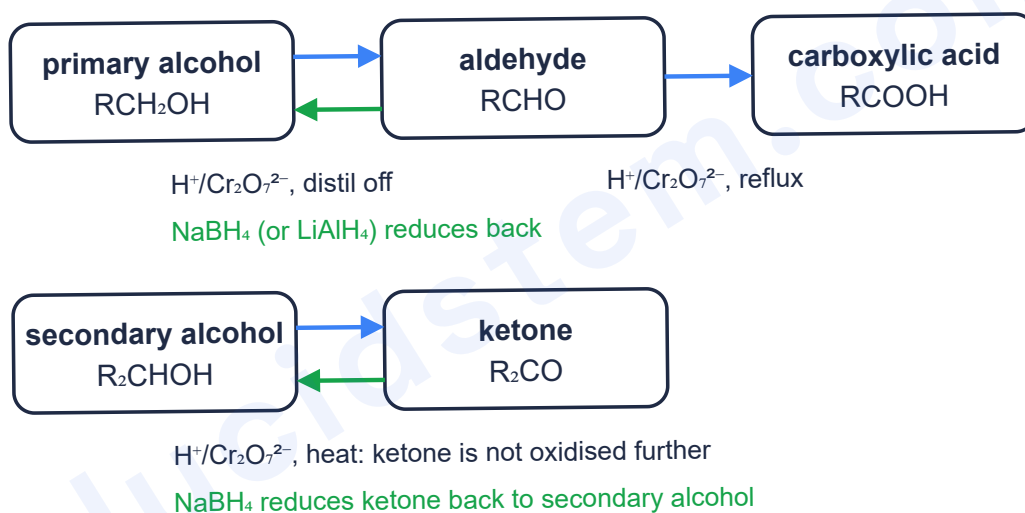


Fig. 1: oxidation with acidified dichromate(VI) goes up the ladder; $NaBH_4$ brings it back down

Primary to aldehyde,
secondary to ketone, NaBH_4
back down.

- ✓ **Aldehyde:** $\text{C}=\text{O}$ at chain end, -al;
ketone: $\text{C}=\text{O}$ mid-chain, -one.
- ✓ **Distil** for aldehyde; **reflux** gives acid.
- ✓ **Ketones** are not oxidised by dichromate.
- ✓ **NaBH_4** + $2[\text{H}]$, back to the alcohol.

Watch out!

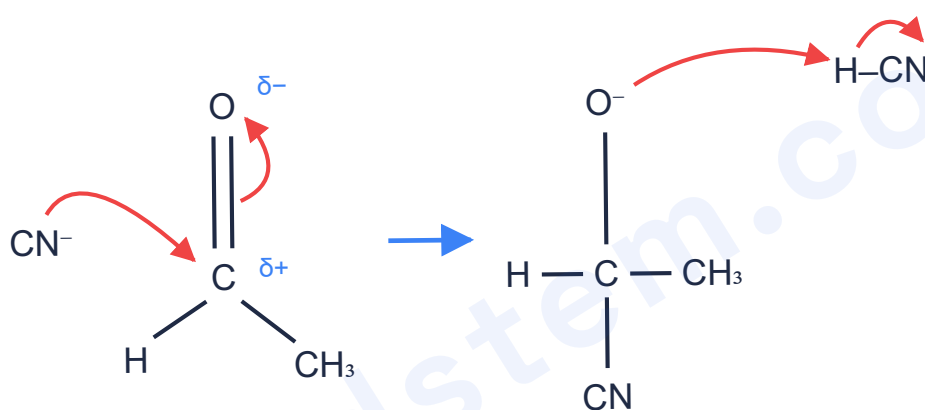
An aldehyde has the $\text{C}=\text{O}$ at the **end** of the chain, a ketone in the **middle**. Distillation gives the **aldehyde**, reflux the **acid**. Ketones are **not** oxidised by acidified dichromate, so a ketone never goes on to an acid. In equations, oxidation uses $[\text{O}]$ and reduction uses $2[\text{H}]$; NaBH_4 reduces $\text{C}=\text{O}$ but does **not** reduce $\text{C}=\text{C}$.

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2 Nucleophilic addition and carbonyl tests

Syllabus 17.1

The $C=O$ bond is polar, so the carbon is δ^+ and is attacked by **nucleophiles**. With **HCN** and a **KCN catalyst**, the CN^- ion attacks the carbon, the π electrons move onto oxygen, and the O^- then takes H^+ from HCN: a **2-hydroxynitrile** forms. Because the $C=O$ group is **planar**, attack from either face is equally likely, so a chiral product is a **racemic mixture**. **2,4-DNPH** gives an orange-yellow precipitate with any aldehyde or ketone. Only aldehydes reduce **Fehling's** (blue to brick-red Cu_2O) and **Tollens'** (silver mirror) and turn acidified dichromate green. Alkaline iodine gives yellow **CHI_3** with the CH_3CO- group.



step 1: the CN^- lone pair attacks the δ^+ carbon;
the π electrons of $C=O$ move onto oxygen

step 2: O^- takes H^+ from HCN, regenerating CN^-

product: $CH_3CH(OH)CN$, 2-hydroxypropanenitrile (racemic)

Fig. 1: nucleophilic addition of HCN to ethanal

Mechanism first, then three tests in order.

- ✓ **HCN/KCN:** CN^- attacks $\text{C}\delta^+$, then O^- takes H^+ .
- ✓ **Planar $\text{C}=\text{O}$:** attack from both faces, racemic product.
- ✓ **2,4-DNPH:** orange ppt for any $\text{C}=\text{O}$.
- ✓ **Fehling's / Tollens':** aldehydes only; CHI_3 for $\text{CH}_3\text{CO}-$.

Watch out!

HCN adds by **nucleophilic** addition, not electrophilic: the attacking species is CN^- , and it bonds through **carbon**. The product is racemic because the $\text{C}=\text{O}$ is **planar**, not because the reaction is $\text{S}_{\text{N}}1$. 2,4-DNPH does **not** distinguish aldehydes from ketones; Fehling's and Tollens' do. Fehling's turns **brick-red**, Tollens' gives **silver**; do not swap them. Propanal gives **no** CHI_3 ; it has no $\text{CH}_3\text{CO}-$ group.